

COLL 1

Improving quantification in liquid cell electron microscopy of materials reactions

Frances M. Ross, fmross@us.ibm.com. IBM T. J. Watson Research Center, Yorktown Heights, New York, United States

With its combination of spatial and temporal resolution in water, liquid cell transmission electron microscopy is a useful tool for measuring reaction kinetics and understanding reaction pathways. It has already provided unique insights into processes such as solution-phase nanoparticle formation and electrochemical deposition. However, a challenge in interpreting liquid cell data is determining the local reaction parameters, for example pH or ion concentration, in the region under observation. In this presentation we discuss the reasons for this uncertainty and consider possible solutions. One key issue is the effect of the imaging beam itself on the solution chemistry. The high radiation dose required for imaging drives radiolytic reactions that chemically change the local liquid environment. We find that simulations can be a helpful tool in understanding the effects of irradiation. We consider, in particular, how the geometry of the electron beam and the interfaces between the liquid and its enclosure might be expected to affect the local chemistry. We discuss how the simulations can be tested and assess future prospects for improving the accuracy with which reaction parameters are known. Better quantification is essential in interpreting liquid cell data on nanoparticle synthesis and related areas, and can even lead to strategies that use beam effects to fabricate more complex nanostructures.

COLL 2

Comparing contrast and electron irradiance limits for soft matter in cryogenic and in-situ liquid-cell electron microscopy

James E. Evans^{1,2}, james.evans@pnnl.gov. (1) K8-93, Pacific Northwest National Laboratory, Richland, Washington, United States (2) Washington State University, Pullman, Washington, United States

In-situ and liquid cell transmission electron microscopy seeks to capture images and dynamics of materials in near-native environments. While maximizing contrast has been the subject of numerous studies on cryogenically preserved samples for cryo-EM, an optimal imaging regime has not been demonstrated empirically for fully hydrated soft matter or biological samples imaged using liquid cell electron microscopy. Additionally, recent questions about the role of the electron beam in driving or damaging physiological events of interest necessitates further investigation of electron beam/cell interactions in the liquid state. In this talk I will present and compare experimentally determined dose dependence of contrast and SNR for multiple liquid cell and cryogenic imaging schemes. This detailed analysis highlights the trade-off between feature detection, dose and resolution for liquid cell (S)TEM and informs the types of experiments and dynamics that can be reasonably interpreted.

COLL 3

Advances in electron imaging and spectroscopy of nanomaterials at cryogenic temperatures

Lena Kourkoutis, lkourkoutis@gmail.com. Cornell University, Ithaca, New York, United States

Controlled solution-based synthesis offers a path towards nanomaterials with designed structure and functionalities. PbSe quantum dots self-assembled into superlattices at liquid-liquid interfaces, for example, can connect epitaxially to nearest neighbors to form confined-but-connected structures in which new electronic states have been predicted. Self-assembly of amphiphilic block copolymers and surfactant molecules in solution is also used to template for the production of tailored nanostructures. The initial steps in these formation processes are often critical. Cryo-transmission electron microscopy (TEM) allows direct observation of specimens snap-frozen in solution and is especially valuable for characterization of the earliest stages of solution-based formation processes. In the first example, I will discuss how cryo-TEM can be used to study the formation process of hybrid organic-inorganic silica nanorings, 10 nm in diameter, formed by the condensation of silica onto organic micelles. We have captured steps in the synthesis of these particles by snap-freezing the structures in solution, revealing the evolution from isolated micelles to aligned silica rings.

The second part of the talk will focus on recent developments that have enabled atomic resolution spectroscopic mapping of nanostructures at cryogenic temperatures. Technical advances in spectroscopic imaging using electron energy loss spectroscopy (EELS) have allowed a material's chemical and electronic structure to be resolved at the atomic scale. While this can now be achieved almost routinely for radiation-hard materials studied at room temperature, cryogenic applications are hampered by the reduced stability of side-entry cryo-holders. This is particularly challenging for spectroscopic mapping as it requires pixel dwell times that are orders of magnitude larger than typical imaging dwell times. Using a spectroscopy-enabled direct electron detector with improved detector quantum efficiency, point spread function, and signal-to-noise ratio compared to indirect, scintillator-based detectors, we demonstrate atom-resolved spectroscopic mapping at liquid nitrogen temperature. Operating at cryogenic temperatures not only allows imaging of nanostructures snap-frozen in solution, but also enables the study of reactive materials and suppresses carbon built-up during imaging which is particularly important for nanoparticles that are not robust to standard cleaning methods.

COLL 4

Using sub-sampled STEM and inpainting to control the kinetics and observation efficiency of dynamic processes in liquids

Nigel D. Browning^{1,2}, *nigel.browning@liverpool.ac.uk*. (1) *Physics, University of Liverpool, Liverpool, United Kingdom* (2) *Mechanical, Materials and Aerospace Engineering, University of Liverpool, Liverpool, United Kingdom*

Many processes in materials science, chemistry and biology take place in a liquid environment. The final outcome of the process is often a result of a series of complicated transients (occurring on timescales of milliseconds to nanoseconds), where a change in the order, magnitude or location in each of the steps in the process can lead to a radically different result. Understanding and subsequently controlling the final outcome therefore requires the ability to directly control and observe the kinetics of these transients as they happen. The spatial and temporal resolution of a transmission electron microscope (TEM) is ideally suited to study these types of processes in liquids provided we can control the experiment sufficiently. First and foremost, we need to maintain a liquid environment in the TEM, which is becoming routine with liquid cell stages from numerous commercial vendors. However, if we wish to acquire a time sequence of images from the same transient event using one of these stages, the effect of the electron beam must now be taken into account. To extract quantitative information free from beam artifacts, we must aim to efficiently use the dose that is supplied to the sample and to extract the most (spatial and temporal) information from each image. For the scanning (STEM) mode of operation, optimizing the dose/data content by the use of sub-sampling and inpainting can increase imaging speed, reduce electron dose by 1-2 orders of magnitude while at the same time compressing the data by the same amount. Here, we discuss the use of inpainting to generate high quality, interpretable images from sub-sampled datasets obtained from crystalline materials – the highly ordered structures allow the physical principles behind inpainting to be identified. New results showing the use of in-situ liquid stages to study nucleation and growth using inpainting will also be presented and the potential insights that can be gained by increasing the image acquisition speed and/or decreasing the electron dose will be described. Importantly for in-situ observations, the kinetic control of the nucleation/growth process using sub-sampling highlights the role of the interfaces in the in-situ cell. Finally, as sub-sampling and inpainting is not limited to STEM, the potential to apply sub-sampling to a wide range of TEM/STEM imaging modes and extract quantitative image information will also be discussed.

COLL 5

Efficient dispersion of oil by blends of food-grade surfactants: Role suggested by Cryo-EM of nanostructures forming at the interface

*David Riehm*¹, *Louis Corcoran*², *R Lee Penn*², *Geoffrey D. Bothun*³, *Srinivasa R. Raghavan*⁴, *Vijay T. John*⁵, **Alon McCormick**¹, *mccormic@umn.edu*. (1) *Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States* (2) *Chemistry, University of Minnesota, Minneapolis, Minnesota, United States* (3) *Chemical Engineering, University of Rhode Island, West Kingston, Rhode Island, United States* (4) *Chemical Biomolecular Engineering, University of Maryland,*

College Park, Maryland, United States (5) Tulane Dept of Chem Bio Engr, New Orleans, Louisiana, United States

For decades, dispersants used for marine oil spills have been formulated with a blend of particular surfactants that are known to ensure effective dispersion at sea. After the Deepwater Horizon event, interest arose about what alternative surfactants might also be suitable to consider for future use. In this presentation we will briefly summarize one promising avenue that has emerged, and nanostructural insights into why specific formulations work well. Cryo-TEM and cryo-SEM both suggest the role played by the dynamic creation of microemulsion-like structures at the oil/seawater interface.

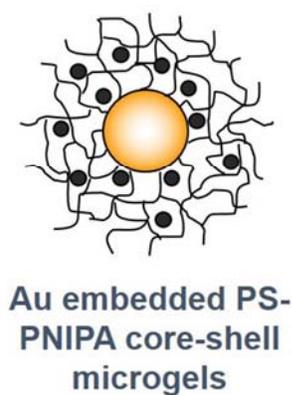
COLL 6

Morphological study of microgel-based colloidal systems by cryogenic transmission electron microscopy (cryo-TEM)

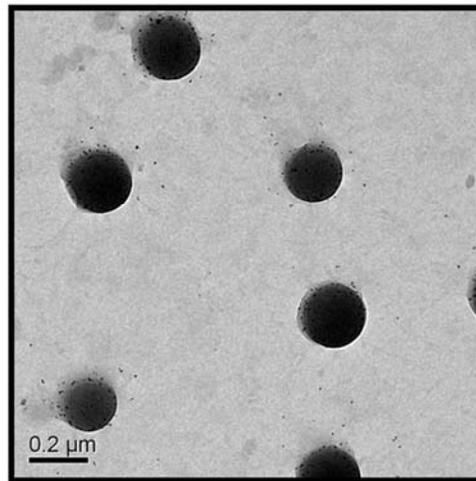
Zdravko Kochovski¹, He Jia¹, Yan Lu^{1,2}, yan.lu@helmholtz-berlin.de. (1) Helmholtz-Zentrum Berlin, Berlin, Germany (2) University of Potsdam, Potsdam, Germany

Cryogenic transmission electron microscopy (Cryo-TEM) is a method of choice to investigate the morphology of colloidal systems in situ. In our research cryo-TEM is demonstrated to be a powerful method to characterize the swollen state of microgels in solution, which is impossible to be observed by normal TEM with dried samples. Environmentally responsive microgels have been subjects of great interest in the last two decades due to their versatile applications in fields like drug delivery, chemical separation and catalysis. As a model system, thermosensitive core-shell microgel particles, in which the core consists of polystyrene whereas the shell consists of a poly (N-isopropylacrylamide) (PNIPA) network, have been used as “nanoreactors” for the deposition of metal nanoparticles (such as Ag, Au, Pd, and Pt). The deposition of the metal nanoparticles inside the microgel shell has been proved by the cryo-TEM images of the composite particles. In addition, by performing the cryo-TEM measurements under different temperatures (both in a swollen state at 15 °C and in a shrunken state at 50 °C). It is found that the thickness of the microgel shell agrees well with the dynamic light scattering (DLS) data.

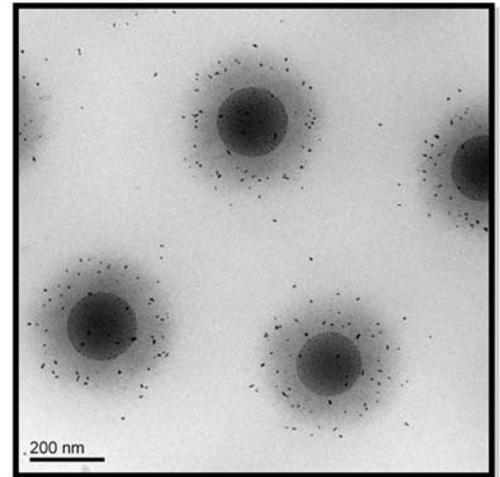
Recently, we have extended the morphological study by cryo-TEM to other colloidal systems, such as colloidal particles made of poly(ionic liquid)s, and sugar-induced protein assemblies. The morphological evolution of polymer particle shape and interior nanostructure can be well presented with cryo-TEM and tomography.



TEM: in the dried state



Cryo-TEM: *in situ*



TEM and cryo-TEM images of the Au nanoparticles embedded in PS-PNIPA core-shell microgels.

COLL 7

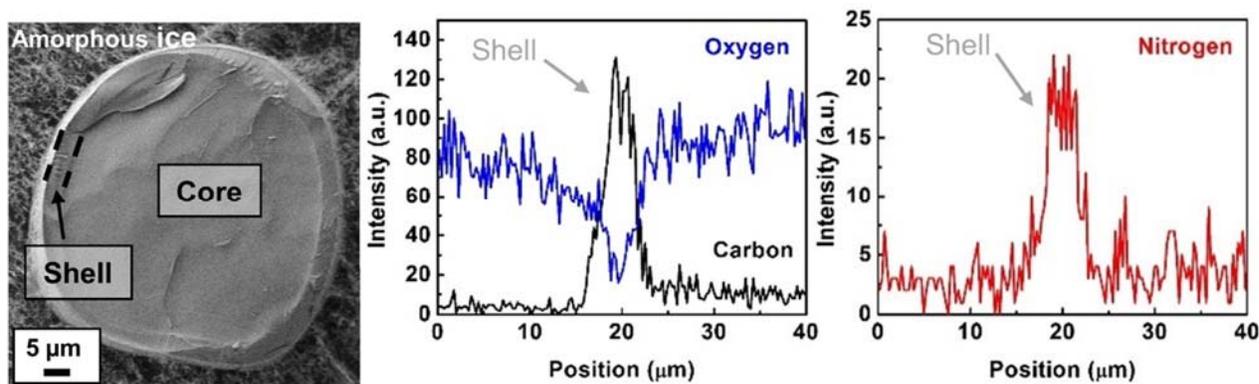
Cryo-SEM imaging and analysis of peptide-complexed microgels

Jing Liang¹, jliang4@stevens.edu, **Xixi Xiao**¹, **Tseng-Ming Chou**², **Matthew Libera**¹. (1) *Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, New Jersey, United States* (2) *Laboratory for Multiscale Imaging, Stevens Institute of Technology, Hoboken, New Jersey, United States*

Anionic microgels have been widely used in drug delivery and surface modification. Their ability to complex with oppositely charged molecules has drawn increasing attention. Many imaging techniques have successfully been used to study microgels including AFM and confocal microscopy, among others. Scanning electron microscopy is particularly appropriate because of its combination of resolution, depth of field, and microanalytical abilities. Characterizing microgels by SEM has, however, been limited because of drying artifacts. Here, we prepare frozen-hydrated samples using high-pressure freezing. We use this approach to study the complexation of cationic antimicrobials within anionic microgels where imaging and X-ray microanalysis (EDS) provide direct evidence for water and counterion release during complexation.

Our experiments use a cationic antimicrobial peptide L5 (+6 charge, 2274 g/mol) and lightly crosslinked poly(acrylic acid) microgels. L5-complexed microgels form a core-shell structure. Significantly different X-ray intensity profiles in the core and the shell indicate differences in local composition. The carbon and oxygen X-ray intensities indicate that the core is highly hydrated while the shell is highly dehydrated. Nitrogen is unique to L5, and a spike in the nitrogen X-ray intensity indicates that the peptide is

localized preferentially in the shell. Also, a depletion of sodium is observed exclusively in the shell. These findings indicate that peptide-microgel complexation drives the local release of both water and sodium counter ions. By studying specimens frozen after various complexation times we find that longer complexation results in a thicker and more dehydrated shell with sufficient mechanical integrity to resist deformation during complete sublimation. The rate of shell thickening decreases such that we observe a maximum thickness of about $\sim 4 \mu\text{m}$. The overall peptide-complexed microgel diameter is $\sim 50 \mu\text{m}$, however, and the much larger core remains hydrated and with no significant changes.



COLL 8

Observing phase transitions of amphiphilic block copolymers in solution by liquid cell TEM

Nathan C. Gianneschi, ngianneschi@ucsd.edu. Chem M/C 0343, University of California, San Diego, La Jolla, California, United States

Amphiphilic small molecules and polymers form commonplace nanoscale macromolecular compartments and bilayers, and as such are truly essential components in all cells and in many cellular processes. The nature of these architectures, including their formation, phase changes, and stimuli-response behaviors are necessary for the most basic functions of life, and over the past half-century, these natural micellar structures have inspired a vast diversity of industrial products, from biomedicines to detergents, lubricants and coatings. The importance of these materials and their ubiquity, have made them the subject of intense investigation regarding their nanoscale dynamics with increasing interest in obtaining sufficient temporal and spatial resolution to directly observe nanoscale processes. However, the vast majority of experimental methods involve either bulk-averaging techniques including light, neutron and X-ray scattering, or are static in nature including even the most advanced cryogenic transmission electron microscopy techniques. Here, we describe *in situ* liquid cell transmission electron microscopy (LCTEM) for the direct observation of the evolution of individual amphiphilic block copolymer micellar nanoparticles in solution, in real time with nanometer spatial resolution. These observations, made on a proof-of-concept

bioconjugate polymer amphiphile, revealed growth and evolution occurring by unimer addition processes and by particle-particle collision-and-fusion events. The experimental approach, combining direct LCTEM observation, quantitative analysis of LCTEM data, and correlated *in silico* simulations, provides a unique view of solvated soft matter nano-assemblies as they morph and evolve in time and space, enabling us to capture these phenomena in solution.

COLL 9

Using ionic liquids to take advantage of the many facets of chitin: Tailor-made high surface area nanofibrous sorbent mats for selective separations of metal ions

Robin D. Rogers^{1,2}, rdrogers@ua.edu, **Gabriela Gurau**^{1,2}. (1) 525 Solutions, Inc., Tuscaloosa, Alabama, United States (2) The University of Alabama, Tuscaloosa, Alabama, United States

We have recently demonstrated that natural biopolymers such as chitin can be electrospun from ionic liquid solution and developed a setup for multi-needle electrospinning of chitin which allows the scale-up of production of nanofibrous chitin mats with controllable and high surface areas. The chitin fibers contain acetylamine functionalities on the surface of the fibers which can be deacetylated and substituted with specific extracting ligands. In our proof of concept, the chitin fiber surfaces were deacetylated using aqueous NaOH and amidoxime ligands were appended to allow the selective sorption of uranium from seawater. These tailor-made sorbents provide both the physical properties of chitin and the functional properties of chitosan, resulting in an advanced material from a biorenewable resource with reduced chemical input. The extracting moiety can be easily changed for selective extraction of a variety of metal ions from aqueous media. While, a sustainable and viable sorbent technology for extraction of uranium from seawater is far from being commercialized, under a Department of Energy Small Business Innovation Research grant, we have proven the general feasibility of the concept. This presentation will discuss the science behind the technology and the progress toward commercial scale operations.

COLL 10

Tuning viscoelastic behavior of particle-stabilized emulsions for enhanced oil recovery applications

Brandy Pilapil¹, bpilapil@ucalgary.ca, **Aseem Pandey**¹, **Maziar Derakhshandeh**¹, **Aika Meimanova**¹, **Aleksandra Govedarica**², **Steven Bryant**¹, **Milana Trifkovic**¹. (1) Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada (2) Chemical and Petroleum Department, University of Calgary, Calgary, Alberta, Canada

Emulsion flooding can be used to enhance oil recovery in under-performing reservoirs, due to its favorable viscoelastic behavior. Tuning this viscoelastic behavior is well-suited

to particle-stabilized emulsions, via tuning of their particle-particle interactions, enabling optimization of EOR processes. However, emulsions with strong particle-particle interactions present a challenge to oil separation processes after oil recovery is achieved. In this work, we will discuss particles with varying size, shape and interaction kinetics and their impact on the flow behavior of the resulting emulsions. These emulsions have been studied using a multi-scale approach, from evaluation of their bulk properties via rheology and creaming height analysis, to microscale characterization of the emulsions via imaging by laser scanning confocal and electron microscopy, and measurement of inter-droplet forces via photonic force microscopy. Particle anisotropy, coupled with fast kinetics of the particle-particle interaction, is shown to enable long-range network formation and emulsions with high storage and loss moduli, while limiting the density of the emulsion networks. Meanwhile, slow kinetics of particle-particle interactions and isotropic shape is shown to enable gradual increases in storage and loss moduli with aging, and densely packed emulsion droplets upon creaming. Finally, progress in the development of methods for separation via flow through porous media will be discussed as a means to deal with these persistent emulsions after their utilization in EOR applications.

COLL 11

Statistics of dispersity of nanosheets by stabilizing oil and water interface

Harish V. Kumar¹, harish.kumar@uconn.edu, Zhihao Zhang¹, Will Dickinson², Sudeep R. Bapat³, Hannes C. Schniepp², Douglas H. Adamson¹. (1) Institute of Material Science, Polymer Program, University of Connecticut, Storrs, Connecticut, United States (2) Department of Applied Science, College of William and Mary, Williamsburg 23187, Virginia, United States (3) Department of Statistics and Applied Probability, University of California Santa Barbara, Santa Barbara 93106, California, United States

Degree of oxidation affects various properties in graphene oxide (GO) sheets. We show that emulsifying a sample of GO separates the sheets into fractions. These fractions vary in extent of oxidation, exfoliation and sheet size. More oxidized GO sheets suspend in a water phase, while the less oxidized material stabilizes the emulsion phase. This in turn provides the ability to control the electrical and thermal conductivity of the GO by making stable emulsions. This fractionation method enables quantifying the oxidation dispersity number of GO (OD) in a batch and can be used to tune the density of oxygen functional groups on the GO sheets in a given sample. Further statistical methods are used to corroborate oxidation dispersity number. We describe this fractionation method, as well as demonstrate the effect controlling the extent of oxidation has on the properties of GO based applications. In addition, we also look into the easier inversion of the sheet stabilized emulsion phases for various applications.

COLL 12

Competition between the hydrolysis-phosphate precipitation reactions in wastewater coagulation

Harsha Ratnaweera, *harsha@nmbu.no*. Norwegian University of Life Sciences, Aas, Norway

Over 70% of municipal wastewater in Norway are treated with coagulation, with over 85% of the resulting sludge used in agriculture. The general targets of wastewater coagulation are maximum removal of particles and phosphates, but downstream processes may demand lower levels of phosphates removal and a lesser reduction of pH. Plant utilisation of phosphates in the sludge, which is a valuable ingredient in commercial fertilizer, is one of the motivations for high use of sludge in agriculture. However, research shows that plant accessibility of phosphates could reduce by over 80% after coagulation, in comparison to biological sludge. The strong chemical bonding between aluminium and phosphate ions is the suspected reason. On the other hand, ever increasing phosphate removal requirements push the plant owners to further increase the already excessively high Al:P dosing ratio, 3-7:1 moles. The result is - even less plant availability, unnecessarily high chemical costs, sludge management costs, and too low pH etc.

The common dosing control often bases on algorithms where the dosage is linearly proportional to the flow. They ignore the influence of particles, phosphates and pH as well as dilution factors due to precipitation and human behaviour. Two concepts that help manage these challenges use (1) improved algorithms to define the optimal dosage and (2) substitute inorganic (Al/Fe) coagulants with cationic polymers for colloids removal, alongside promoting the phosphate precipitation reaction to hydrolysis process.

An innovative dosing control concept can document reduced dosage by over 30%. A combination of this process and substitution of inorganic coagulants with cationic polymer helped manage the increase of plant availability from 20% to 50%, although even higher yields were anticipated. The competition of the hydrolysis and phosphate precipitation reactions are identified as the limiting reason. The relative concentration of colloids/particles and pre-polymerisation ratio of coagulants are identified as influential parameters. Theoretical options to favour the phosphate precipitation process to hydrolysis will be discussed.

COLL 13

Practical approaches to modified “smart” fabrics for oil/water separation from stabilized emulsions

Morgan Lehtinen, *11mjl18@queensu.ca*, *Zijie Wang*, *Guojun Liu*. Dept Chemistry, Queens Univ, Kingston, Ontario, Canada

Oil-in-water emulsions are present in many industrial processes including oil refinery and water treatment. For oil recovery in Alberta, hot steam is used to remove crude oil from the sands, yielding an oil-in-water emulsion. The current separation processes to remove oil from such emulsions is tedious and wasteful of energy and resources. Our

group recently reported the use of asymmetric cotton fabrics as filters to practically and efficiently separate oil from surfactant stabilized oil-in-water emulsions. First, polymers are grafted onto different sides of cotton fabrics to yield Janus filters. These asymmetric filters are modified with polymers to be hydrophilic on one side and superhydrophobic on the other. Upon contact with an emulsion, the hydrophilic side causes the oil droplets in water to coalesce and the coalesced oil globules then selectively permeate the superhydrophobic side, leaving the water and surfactant behind. To ensure the greenness of the fabric modification process, water-based formulations have been used to coat fabrics. The formulations have also been used to modify metal meshes and the resultant meshes are then used for crude oil separation. This work explores the interfacial chemistry behind the use of cotton filters for effective oil separation from oil-in-water emulsions for industrial applications.

COLL 14

Micelle based separations: From small molecules to proteins to nanoparticles

Ramanathan Nagarajan, ramanathan.nagarajan.civ@mail.mil. Natick Soldier RDEC, Natick, Massachusetts, United States

Micelle based chemical separations was proposed many years ago based on theoretical models developed for the phenomenon of solubilization in micelles. The theory predicted that benzene will be solubilized selectively over hexane when their binary hydrocarbon mixture is contacted with surfactant micelles. Experiments showed that selectivity for benzene over hexane extended from about 2 to 4 depending on the composition of the hydrocarbon mixture and the type of the surfactant. The origin of selectivity was identified as arising from the molecular size and interfacial activity of the solubilize. In searching for ways to enhance the selectivity, block copolymer micelles were found to provide significant enhancement in selectivity between aromatic and aliphatic hydrocarbons as well as large capacities of solubilization per unit mass of the micelle. The origin of selectivity was not interfacial activity as in the case of surfactants, but the interactions between the solubilize and the hydrophobic block of the copolymer. The molecular size effect becomes less important compared to the molecule-hydrophobic block interactions. Selective extraction has also been demonstrated using reverse micelles which solubilize proteins based on their molecular size and surface charge. In these systems, the thermodynamically anticipated selective extraction does not often work because of kinetic barriers. However, by manipulating the interface of the micelle by the small addition of an alcohol, the kinetic barrier can be overcome and the extraction process is controlled by equilibrium factors. Highly selective protein uptake and efficient back extraction from reverse micelles have been demonstrated for acid proteases pepsin and chymosin. Beyond the application to small organic molecules and proteins, the micellar solubilization can also be used to electively fractionate nanoparticles. Theoretical modeling of solubilization of carbon nanotubes by block copolymer micelles showed that nanotube radius and nanotube – hydrophobic block interactions control the selective solubilization of the nanotubes making possible potential separations based on size and chirality of nanotubes. These theoretical results

remain to be exploited in practical separation schemes for nanotubes and other nanomaterials.

COLL 15

Enhancement of the solid-liquid separation in oil sands tailings treatment using silica nanoparticles

Aleksandra Govedarica, *aleksandra.govedaric@ucalgary.ca*, **Sharukh Shamim**, *sharukh.shamim@ucalgary.ca*, *Milana Trifkovic*, *Ayesha Abid*. *Chemical and Petroleum Engineering Department, University of Calgary, Calgary, Alberta, Canada*

The densification of the stable particulate dispersions resulting from the oil sands extraction is commonly achieved via polymer flocculation. Even though kinetics of the initial water release is fast, polymer flocculants as standalone treatment agents have been limited by the inherent variability of the tailings streams. Moreover, the polymer chain binding and bridging between mineral particles, which vary in size, charge density and surface reactivity, often results in the formation of nonuniform flocs and unsatisfactory long term densification. In recent years, the use of nanoparticles has gained momentum as an alternative tailings reclamation technique. In this work we present a novel treatment method using bare silica nanoparticles, which resulted in the destabilization of the tailings systems and allowed the formation of three distinct layers in the resulting sediment. Each layer varied in solids content and the consequent yield stress. The sediment properties were studied by relating the microstructural characteristics, examined by the scanning electron and confocal laser microscopy, to its rheological properties. In order to overcome the drawbacks of the slow dynamics of sediment formation with silica treatment, we studied the synergistic effect of silica and polymer flocculation. Here, the silica nanoparticles were found to enhance the polymer flocculation by imparting the favorable surface chemistry and the resulting sediment compactness, while the polymer bringing enabled the necessary treatment dynamics to take place. The hybrid approach presents a promising new route towards the efficient tailings treatment.

COLL 16

Nanoscale view of assisted ion transport across the liquid-liquid interface

Mark L. Schlossman, *schloss@uic.edu*. *Univ of Illinois, Chicago, Illinois, United States*

During solvent extraction, amphiphilic extractants assist the transport of metal ions across the liquid-liquid interface between an aqueous ionic solution and an organic solvent. Investigations of the role of the interface in ion transport challenge our ability to probe fast molecular processes at liquid-liquid interfaces on nanometer length scales. Recent development of a thermal switch for solvent extraction has addressed this challenge, which has led to the characterization by X-ray surface scattering of interfacial intermediate states in the extraction process. We find that trivalent rare earth ions, Y(III)

and Er(III), combine with DHDP extractants to form inverted bilayer structures at the interface; these appear to be condensed phases of small ion-extractant complexes. The stability of this unconventional interfacial structure is verified by molecular dynamics simulations. The ion-extractant complexes at the interface are an intermediate state in the extraction process, characterizing the moment at which ions have been transported across the aqueous-organic interface, but have not yet been dispersed in the organic phase. In contrast, divalent Sr(II) forms an ion-extractant complex with DHDP that leaves it exposed to the water phase; this result implies that a second process that transports Sr(II) across the interface has yet to be observed. Calculations demonstrate that the budding of reverse micelles formed from interfacial Sr(II) ion-extractant complexes could transport Sr(II) across the interface. Our results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction selectivity and kinetics.

COLL 17

Controlled architecture of amine ligands decorated glass fiber/poly(glycidyl methacrylate) composites via surface-initiated ICAR ATRP mediated by mussel-inspired polydopamine chemistry for uranium extraction from seawater

Wenqing Wang¹, wenqingwang@tsinghua.edu.cn, Gang Ye², Jing Chen³. (1) Institute of Nuclear and New Energy technology, Tsinghua University, Beijing, China (2) Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, China (3) Tsinghua Univ., Beijing, China

A new material system, organic amine ligands decorated polymer brushes from surfaces of glass fibers, was achieved for effective adsorption of uranium ions by integrating surface-initiated atom transfer radical polymerization (SI-ATRP) technique with the mussel-inspired polydopamine (PDA) chemistry. Firstly, homogenous PDA layer were firstly deposited onto glass fiber mats (GFMs), facilitating the anchoring of ATRP initiators. Then propagation of poly(glycidyl methacrylate) (PGMA) brushes from the GFMs were then initiated by using the initiators for continuous activator regeneration (ICAR) ATRP method. PGMA brushes with defined structure, grafting density (5 wt.% ~ 25 wt.%) and well preservation of chain end-functionality could be obtained by reducing radical initiator ratio and using a high dilution strategy (solvent: monomer=10:1 (V:V)). And, a narrow distribution of molecular weight ($PDI \leq 1.2$) could be attained within reduced polymerization time. The abundant reactive epoxy groups in the PGMA brushes provided an ideal platform for post functionalization of the obtained composites PCGFMs. Diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) ligands, were separately introduced to PCGFMs. With the number of amino increasing, amine grafting density of the functionalized composites PCGFMs-NH₂ increased. The adsorption behavior of PCGFMs-NH₂ toward uranium was fully investigated. In experimental conditions, pH value of 5.0 and lower temperature were beneficial for the adsorption of uranium onto PCGFMs-NH₂. Besides, PCGFMs-NH₂ performed well in uranium extraction from natural seawater (pH=8.5, Conc.=2 ppb) with a removal ratio up to 75.9%. With amine grafting density increasing,

a little difference in uranium adsorption capacity was observed in simulated solution but uranium removal ratio kept increasing in natural seawater. This could be explained by the protonation in weak nitric acid medium. The synthetic strategy established in this work provided an opportunity for broadening functional fibrous extraction substrates for uranium adsorption.

COLL 18

Regulatory science and considerations for drug products containing nanomaterials: FDA perspective

Celia Cruz, celia.cruz@fda.hhs.gov. CDER, FDA, Silver Spring, Maryland, United States

Nanotechnology can be used in a broad array of FDA-regulated products and is used to develop products in which nanomaterials serve a variety of functions, for example as active ingredients, carriers loaded with an active ingredient, or inactive ingredients. The inclusion of such materials may result in product attributes that differ from those of products that do not contain such materials, and thus may merit particular examination. This presentation will highlight the regulatory considerations for the development and review of drug products containing nanomaterials. These regulatory considerations include the use of advanced analytical methods for adequate characterization of the nanomaterial, in context of its intended use and function in the drug product. We will also explore the risk based-framework for development and regulatory review of drug products containing nanomaterials, in the recently published Draft Guidance For Industry: Drug Products, Including Biological Products, that Contain Nanomaterials. Lastly, we will discuss the contribution of regulatory research to the advancement of nanotechnology in drug products by furthering FDA's understanding of the physicochemical properties of nanomaterials and their role in drug product quality, safety and efficacy.

COLL 19

Engineering and development of novel antibody-directed nanotherapeutics for the treatment of cancer

Daryl C. Drummond, ddrummond@merrimack.com. Research, Merrimack Pharmaceutical, Lincoln, Massachusetts, United States

Antibody directed nanotherapeutics represent a promising next generation antibody drug conjugate technology with several important characteristics. First, the targeting ligand is only indirectly conjugated to the active drug payload through a nano-sized liposomal carrier and not covalently to the antibody itself. Second, the liposomal nanocarrier of approximately 100-120 nm in size can encapsulate a sizeable payload of 20-150,000 drug molecules, allowing it to be applicable to a wide range of drugs with more standard potencies than observed for conventional ADCs. The size of the

nanocarrier also enables a second level of targeting due to the enhanced permeability and retention effect and its more restricted distribution into healthy tissues. Here we demonstrate the potential of this platform through the engineering of an EphA2-antibody targeted nanotherapeutic encapsulating a novel docetaxel prodrug (MM-310). MM-310 shows selective targeting of EphA2+ cancer cells and preferential uptake in solid tumors relative to an IgG Ab against EphA2 (C10). The slow and sustained release of the docetaxel prodrug enables a limited systemic exposure to the active docetaxel and a dramatic reduction in neutropenia, the dose-limiting toxicity of free docetaxel. The sustained tumor exposure results in a significant increase in antitumor activity in multiple xenograft tumor models compared to free docetaxel, and the ability to be more readily combined with a range of combination partners. Finally, we describe the use of nano-sized imaging agents to predict the distribution and activity of both targeted and non-targeted nanotherapeutics.

COLL 20

Metrological challenges and issues related to measurement of nanoparticle size

Debra Kaiser, debra.kaiser@nist.gov. Material Measurement Laboratory, NIST, North Potomac, Maryland, United States

It is well-established that nanoparticle size has a great influence on the biological properties of particles, including those used in nanomedicine. Nanoparticle size determination is inherently complicated, as each technique measures a different aspect of size. For example, dynamic light scattering measures the average hydrodynamic diameter of a population of particles while atomic force microscopy measures the height of individual particles. This concept is well-illustrated by NIST's gold nanoparticle reference materials, for which particle size was measured by six different techniques. Other metrological challenges specific to nanomedicine will be discussed.

COLL 21

Orthogonal approaches to sizing of nanomaterials in the pharmaceutical environment

Silvia Sonzini¹, silvia.sonzini@astrazeneca.com, Kevin Treacher², Zahid Nazir³, Sanyogitta Puri¹. (1) Advanced Drug Delivery, Pharmaceutical Sciences, IMED Biotech Unit, AstraZeneca, Cambridge, United Kingdom (2) Global Product Development, Pharmaceutical Technology & Development, AstraZeneca, Macclesfield, United Kingdom (3) Early Product Development, Pharmaceutical Sciences, IMED Biotech Unit, AstraZeneca, Macclesfield, United Kingdom

Nanomaterials are becoming more and more prominent within the pharmaceutical companies' research and development programs and nanomedicines have recently shown valuable progress towards clinical trials. In a fast pace world where the market seems saturated by small molecules that for certain indications, such as oncology, often

don't offer enough selectivity, the use of nanoparticles as novel drug delivery carriers offers a chance to improve therapeutic index and opening access to target the intracellular domain of diseased cells. Whilst these systems are particularly attractive for their safety and efficiency profiles, their characterization both *in vitro* and *in vivo* presents several challenges. Nanoparticles are relatively large compared to a small molecule, and often polydisperse. Thus, investigating the physical-chemical properties of a nanomaterial involves a diverse spectrum of analytical techniques. Herein, we will especially focus on particle sizing of two nanoplatfoms currently in AstraZeneca, dendrimers and polymeric nanoparticles (PNPs). Both systems have been designed to overcome solubility issues of the active pharmaceutical ingredients (APIs) whilst also prolonging systemic circulation and target tissue distribution. However, the two platforms are very different in their properties, such as hydrodynamic radius (~7 nm and ~50 nm, respectively) and aggregation propensity, drug release rate modulation and stability. To fully characterize these systems, we present their sizes measured through several orthogonal techniques based on light scattering, Taylor dispersion analyses and microscopy; in addition, the influence of media and API properties on the nanomaterials colloidal behavior will also be discussed along with the importance of applying both in batch and separation modes to obtain an all rounded picture of these challenging systems.

COLL 22

At-line DLS for real-time monitoring of particle size in a nanoemulsion process

Max Mahoney, *mmahoney5290@gmail.com. Nanomedicine Development and Manufacturing, Pfizer, Somerville, Massachusetts, United States*

ACCURINS® are a Pfizer-owned, clinically-validated, targeted nanoparticle technology developed from the legacy BIND Therapeutics platform. ACCURINS contain a therapeutic payload and are designed to target tumors at three levels: tissue, cellular, and molecular. They combine this triple targeting with a prolonged circulation time to concentrate the therapeutic payload at the disease site, where it is then released in a controlled manner. ACCURINS® are manufactured by a nanoemulsion process that uses high pressure homogenization to shear organic droplets dispersed within an immiscible aqueous phase. Control over the dispersed droplet size distribution is critically important to determine the final size distribution of the drug product and other quality attributes.

To enable this control, we have installed an at-line dynamic light scattering (DLS) instrument into our homogenization train to continually monitor the droplet sizes being produced. The at-line system removes a sample from the process, dilutes the sample to avoid multiple scattering effects, and measures the sample to determine particle size and polydispersity. Sample measurements can be acquired approximately every 5 minutes, providing continuous particle size information to the process engineers monitoring the manufacturing operation and allowing for feedback control of the process to adjust the particle size.

We will present the details above, discuss the implications the at-line DLS has had on

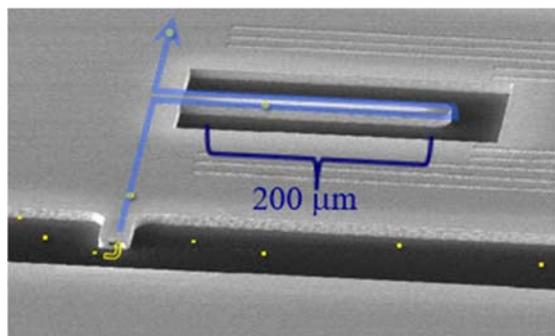
our process, and view experimental results from different manufacturing campaigns. Finally, we will analyze historical issues and discuss future considerations to improve on this process analytical control.

COLL 23

Resonant mass measurement technique for subvisible particle characterization: Applications in the nanomedicine arena

Bob Coyne, *bob.coyne@malvernpanalytical.com*, **Judith Hadley**, *Malvern Panalytical, Westborough, Massachusetts, United States*

One of the most recent entries into the world of nano materials characterization is the Archimedes instrument from MalvernPanalytical. This instrument uses a proprietary technology called Resonant Mass Measurement (RMM) based on a MEMS sensor to measure mass with attogram sensitivity. In addition to measuring the size of nanoparticles, the sensitivity of RMM enables some interesting characterization measurements such as quantifying particle loading, and characterizing core-shell nanoparticle structures. Recently Archimedes has been used to verify the presence of nanobubbles in the contrast imaging area and to help understand the role that nanobubbles play in both imaging and therapeutics. Based on buoyant mass measurements (hence the name), Archimedes also counts and sizes particles separately according to their buoyant properties within the fluid in which they are measured. This presentation will discuss the Resonant Mass Measurement technology, how it works and present some examples of its unique measurement capabilities in characterizing nanoparticles in the nanomedicine application space.



Archimedes MEMS sensor

COLL 24

Innovations in single particle and single cell ICP-MS – Accurate measurements of particle number in cells

Chady Stephan, *chady.stephan@perkinelmer.com*, **Ruth Merrifield**, *PerkinElmer, Woodbridge, Ontario, Canada*

Since the release of SP-ICP-MS by PerkinElmer in 2014 it has become a staple analysis tool for particle counting and sizing in the nanoparticle world. It is now widely accepted as a technique for nanoparticle analysis in a wide variety of industries from environmental, food, semi con and health sciences with a standardized method released by ISO (19590:2017) and another coming from ASTM (WK55613) in the near future. Although the technique is now seen as a standard method, the technology, applications and analysis techniques are still rapidly advancing. Here we would like to talk about recent advances in SP-ICP-MS to include: quantifiable dual analyte analysis enabling particle source identification, clustering techniques enabling enhanced particle size detection, the use of All Matrix Solution (AMS) inline dilution to prevent NP transformations from sample preparation and Single Cell ICP-MS (SC-ICP-MS) a technology which is capable to quantitatively measure the metal content in individual cells, unveiling new capabilities to study intrinsic metals and the uptake of dissolved (ionic) and nanoparticulate metals into cells, providing new insights into drug delivery, toxicity assessment, bioavailability, and bioaccumulation mechanisms using the NexION series ICP-MS.

COLL 25

Is that peak real? Separating truth from fiction in particle analysis

Jean-Luc Fraikin, jeanluc.fraikin@spectradynellc.com, Franklin Monzon, Lew Brown. Spectradyne, Torrance, California, United States

Does your sample show a peak in the particle size distribution when measured by optical methods such as Dynamic Light Scattering (DLS) or Nanoparticle Tracking Analysis (NTA)? Do you feel confident that the peak you see is an accurate representation of the true particle size distribution in your sample?

Light scattering techniques are heavily biased towards detection of large particles because the intensity of scattered light increases as the 6th power of particle diameter. While these techniques are still frequently used, awareness is growing that they commonly report misleading results—even showing a false peak in the particle size distribution when in fact none exists. In order to properly characterize submicron particle distributions, researchers need innovative orthogonal techniques.

Spectradyne's nCS1™ is a non-optical, electrical technique that is truly orthogonal to light-based methods and accurately measures the size and concentration of particles in a sample. The technology is a practical, easy-to-use implementation of resistive pulse sensing (RPS, commonly known as the Coulter principle), a method that has been trusted for decades for characterizing large particles. Spectradyne's implementation of RPS counts and sizes particles as small as 50 nm, independently of particle material or sample polydispersity. The nCS1 delivers accuracy in particle size and concentration at the nanoscale that is unprecedented in a bench-top instrument.

In this presentation, a brief overview of Spectradyne's Microfluidic RPS (MRPS™) is

given, and case studies are presented that compare the nCS1 to DLS, NTA, and electron microscopy. These case studies expose the misleading results reported by light scattering technologies in such diverse samples as protein formulations, extracellular vesicles, and nanomedicines. The results emphasize what many scientists increasingly appreciate: As materials become more complex and nanoparticles are more widely deployed, new particle metrology is required to keep up with the demands of materials characterization.

COLL 26

What does it take to accurately measure concentration of particles in colloids?

Jan K. Tatarkiewicz, kuba.tatarkiewicz@mantainc.com. MANTA Instruments, Inc., San Diego, California, United States

We will discuss influence of various experimental parameters such as counts and investigated volume that are determined by different methods to measure concentration of particles in colloids, especially in poly-disperse and poly-material ones. We will compare principles of measurements for established technologies like transmission electron microscopy (TEM), flow cytometry (FC), resistive pulse sensing (Coulter) and nanoparticle tracking analysis (NTA) as well as improvements introduced to the latter by multispectral advanced nanoparticle tracking analysis (MANTA). We will discuss details of experimental methods and calibration of ViewSizer® 3000 instrument that are based on already issued patents. Also, computational details of data processing will be presented and compared with “proprietary” methods (i.e. not disclosed to customers) used by other manufacturers of nanoparticle sizing instruments. We will present experimental results obtained for standardized samples and for a wide variety of colloids encountered in research studies in diverse fields of interest.

COLL 27

Photothermal effects of plasmonic nanoparticles: fundamentals and applications

Naomi J. Halas, halas@rice.edu. Rice Univ Ece Dept, Houston, Texas, United States

Plasmonic nanoparticles are well known for their large resonant optical cross-sections that are much larger than their physical cross-sections. A major energy dissipation channel for plasmon decay is photothermal heating. We will discuss photothermal heating in the context of collective photothermal effects and the outcomes of applications of plasmonic nanoparticle-based photothermal heating from cancer therapy, now in clinical trials, to solar vapor generation, with applications ranging from portable autoclaves to portable desalination.

COLL 28

Janus Fe₃O₄-Au magnetic-plasmonic nanoparticles for sensing, hyperthermia, and molecular imaging

Javier Reguera^{1,2}, jreguera@cicbiomagune.es, Dorleta Jimenez de Aberasturi¹, Judith Langer¹, Malou Henriksen-Lacey¹, Luis Liz Marzan^{1,2}. (1) CIC biomaGUNE, San Sebastian, Guipúzcoa, Spain (2) Ikerbasque, Bilbao, Spain

A plethora of new inorganic nanoparticles has appeared in the last years boosting the development of a wide variety of technological areas. Among them, noble metal nanoparticles are prominent examples as they allow manipulation and control of light through their plasmonic properties. Another recognized type is the one formed by ferro- and ferrimagnetic materials, such as iron oxide, that at small size shows superparamagnetism enabling its manipulation with external magnetic fields and the subsequent re-dispersion in its absence.

Janus nanoparticles (those with two chemically different regions) have emerged as exceptional candidates for many applications. Their strong interaction with interfaces has been used in applications ranging from emulsified nanoreactors to filtering nanomembranes. Their unique anisotropy has been applied in antireflection surfaces, electronic displays, nanojets, or just as building block for more complex molecular colloids and supracrystals. They also offer extraordinary potential in biomedicine where they can mimic natural biomolecules, produce directed interactions with cell membranes, and offer selected regions with high number of interaction points while keeping multiple functionalities.

Here, we report the synthesis and characterization of novel Janus Au-Fe₃O₄ star-sphere nanoparticles. They show superparamagnetism and a high plasmonic absorption at the near-IR (first biological transparency window). Different versions of nanoparticles have been synthesized through two consecutive seed-mediated-growth steps by varying the precursor to seed ratios. The obtained synthesized nanoparticles are highly uniform and show good colloidal stability in water, PBS, and cell media. Their combination of properties makes them highly versatile and potential candidates to many applications. Here, we report on their characterization in analytical sensing using surface-enhanced Raman spectroscopy (SERS), plasmonic hyperthermia, and multimodal imaging including cell imaging in dark and bright field, multiplexed SERS mapping, magnetic resonance imaging (MRI) computed tomography (CT) and photoacoustic imaging. The synthesized nanoparticles have shown to be excellent nanoproboscopes in all techniques with clear advantages provided by the Janus configuration. These results open the doors to their use in many applications, including the generation of integrated nanodevices for a multi-angle approach in well controlled and efficient biomedical applications.

COLL 29

Photothermal response of gold nanorods prepared using A CTAB-aromatic additive system

Iris W. Guo, iguo@sfu.ca, Michael C. Wang, Idah Pekcevik, Byron D. Gates. Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada

Anisotropic metal plasmonic nanomaterials, such as gold nanorods, are attractive for a variety of applications that utilize localized heating effects that result from photothermal processes. Through photothermal processes, the gold nanorods can be used as a platform to trigger small molecule release and/or localized cell death. These nanomaterials have an advantage that their localized surface plasmon resonance properties are coupled to both their shape and aspect ratio; tuning the physical features of gold nanorods during their synthesis is a simple means to control their optical properties and, thus, photothermal efficiencies over a variety of electromagnetic energies. The second component of utilizing gold nanorods as vehicles for photothermal triggered events is to understand (and control) the evolution of their size and shape under photothermal conditions. High photon fluxes during photothermal processes are known to induce structural and morphological changes to gold nanorods, but these changes are dependent on a number of factors that include the surface chemistry of these materials. Understanding the potential instability of gold nanorods is vital to retain their plasmonic properties for prolonged or repeated use in photothermally triggered processes. The study discussed here introduces the photothermal response of gold nanorods prepared by a modified seed mediated synthesis that uses a mixture of surfactants to control and direct the growth of the nanorods. The photothermal response will be discussed based on the results of a combined analysis from extinction spectroscopy, electron microscopy techniques (e.g., TEM, EDS, and HR-TEM), and statistical analyses.

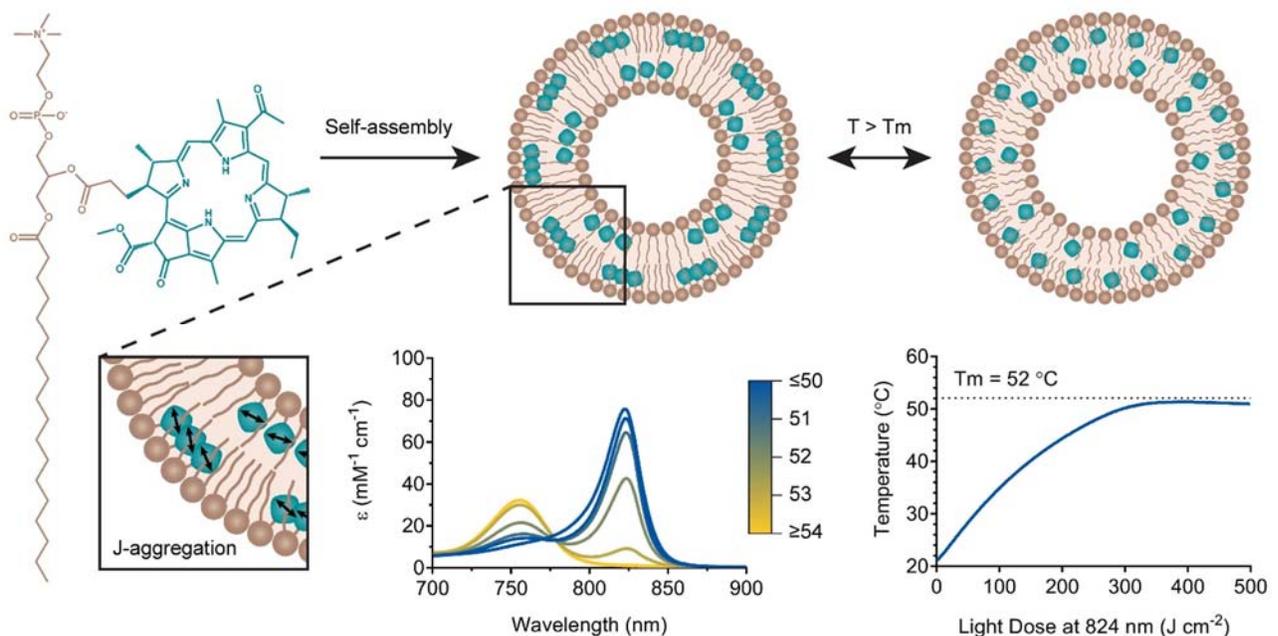
COLL 30

Photoacoustic alternative to MR thermometry during photothermal therapy

Danielle M. Charron^{1,2}, d.charron@mail.utoronto.ca, Hilde H. Buzzá³, Robert Weersink^{2,5}, Gang Zheng^{2,4}. (1) Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada (2) Princess Margaret Cancer Centre, University Health Network, Toronto, Ontario, Canada (3) São Carlos Institute of Physics, University of São Paulo, São Paulo, Brazil (4) Department of Medical Biophysics, University of Toronto, Toronto, Ontario, Canada (5) Department of Radiation Oncology, University of Toronto, Toronto, Ontario, Canada

Photothermal therapy using laser light and exogenous photoabsorbers has an important clinical limitation: it must be performed under the guidance of magnetic resonance thermometry, which is cumbersome and expensive. For photothermal therapy to be widely adopted, an alternative imaging method is a clinical must-have. Photoacoustic imaging is a possible solution when combined with a photoabsorber that is also a photoacoustic sensor for temperature. To generate a thermally responsive optical system, the natural photoagent bacteriopheophorbide *a* was conjugated to a phospholipid (BChl-lipid) and self-assembled into liposomes. Within the lipid shell of

these nanoparticles, BChl-lipid aligns head-to-tail, shifting the Q_y (S_0 - S_1) absorption band from 750 nm to 824 nm and increasing the peak extinction 2-fold, all characteristics of J-aggregation. The liposomal BChl-lipid is also fluorescently quenched by ~90%, and is, therefore, photothermally and photoacoustically active. As a nanostructure-dependent phenomenon, BChl-lipid J-aggregation is influenced by lipid membrane fluidity and so the absorption peak at 824 nm is lost when the lipid transition temperature, defined by the lipid tail length, is exceeded. Loss of the ratiometric photoacoustic signal at 824 nm / 750 nm during laser irradiation at 824 nm indicates that the target temperature has been reached. Optical and structural studies demonstrate that BChl-lipid J-aggregation is a dynamic system, with temperature influencing light-to-heat conversion before the transition temperature is reached. Further, protein adsorption in biological environments also impacts the J-aggregate optical stability and sharpness of the thermal transition, which can be moderated through control of the liposome formulation. Application of this responsive photoabsorber to photothermal therapy with real-time photoacoustic imaging guidance will be discussed within this physical context, and guidelines for its integration into current biophotonics methods will be considered.



COLL 31

Conversion of light energy into heat and hot electrons using hybrid nanostructures with plasmonic hot spots

Alexander Govorov, govorov@ohio.edu. Ohio University, Athens, Ohio, United States

Metal nanocrystals exhibit strong plasmon resonances and have the ability to absorb and scatter light very efficiently. Our study concerns special designs of plasmonic nanostructures with electromagnetic hot spots, where the energy of incident light

concentrates. Overall plasmonic nanostructures with hot spots demonstrate strongly amplified energy-related effects. (1) Using such nanostructures, one can strongly enhance optical generation of heat and also confine high photo-temperatures in small volumes. (2) Plasmonic hot spots efficiently generate energetic electrons, which can be used for photochemistry and photodetection. (3) Plasmonic metamaterial absorbers and bolometers with a chiral geometry exhibit giant photothermal circular dichroism. In such structures, the photoinduced temperature strongly depends on the helicity of circular-polarized incident wave.

COLL 32

Controlling the cellular uptake of plasmonic nanoparticles by host-guest interactions for optical hyperthermia

*Jesús Mosquera Mosquera*¹, *jmosquera@cicbiomagune.es*, *Isabel García*¹, *Malou Henriksen-Lacey*¹, *Luis Liz Marzan*². (1) *Bionanoplasmonics, CICbiomaGUNE, San Sebastián, Donostia, Spain* (2) *CIC biomaGUNE, Donostia - San Sebastian, Spain*

Gold nanoparticles (AuNPs) can absorb near infrared light, provoking photothermal heating. Due to this fact, they are promising tools for creating localized heating that can be used for ablation of tumors. Although AuNPs has tendency to accumulate in tumors due to the enhanced permeability and retention (EPR) effect, they are usually rapidly trapped by macrophages/phagocytes, and then remained localized in the liver. Therefore, controlling the *in vivo* location of nanoparticles remains one of the main challenges for the application of this technology.

We have recently described a supramolecular chemistry approach to control the cellular uptake of small AuNPs (2 nm) based on a host-guest interaction between pyranine and an oligocationic covalent cage. We proved that attaching enough pyranine molecules onto AuNPs hamper their cell internalization owing to the build-up of a high negative potential on their surface. Addition of cage switches the negative surface into positive, and induces the cellular uptake of AuNPs.

The former strategy can be also applied to control the internalization of much larger plasmonic nanoparticles. For example, the cationic cage induces the cellular internalization of gold nanorods, which are ideal for hyperthermia applications, even in the presence of complex biological media. Importantly, this fact could enable the spatio/temporal control of AuNPs *in vivo*. Furthermore, preliminary studies have also showed that when AuNPs are inside cells they can kill them more efficiently than when they are in the cellular environment.

COLL 33

Hybrid nanoscale architectures: Plasmonic and magnetic induced heating applications

Simona Hunyadi Murph, *simona.murph@srl.doe.gov*. *Savannah River National Lab, Aiken, South Carolina, United States*

Hybrid nanoscale architectures often exhibit improved physical and chemical properties over their single-component counterparts, and hence are potentially useful in a broader range of applications. This presentation will summarize recent advances in the design and fabrication of hybrid metal-metal oxide nano-architectures for energy storage and catalytic applications. The development of a hydrogen-based economy relies on the scientists' ability to develop hydride materials with high storage capabilities that can sustain a fast, safe and long-lasting hydrogen charge-discharge performance. In this presentation, we'll demonstrate the release of energy, in the form of hydrogen stored in a hydride-magnetic (Pd-Fe₂O₃) nanomaterial, via an induced magnetic field. We found that, in the presence of a magnetic field, the Fe₂O₃ component of the Fe₂O₃-Pd hybrid material act as a local "hot-spot" and heat up the surrounding environment by hysteresis loss or relaxation mechanisms. The amount and rate of gas release was tuned by adjusting the strength of the magnetic field applied. Additionally, Fe₂O₃ nanoparticles of different shapes: spheres, rings, and tubes were decorated with gold nanoparticles (AuNPs) and evaluated for their ability to catalytically reduce 4-nitrophenol (4-NTP). Remarkably, it is found that Fe₂O₃-Au nanoparticles are more efficient catalysts than AuNPs because they can achieve the same, or better, catalytic reaction rates using significantly smaller quantities of Au, which is the catalytically active material. Furthermore, the Fe₂O₃-Au nanoparticles and AuNPs are found to efficiently transduce heat from light through plasmonic absorbance, and this phenomenon is exploited to demonstrate the photothermal catalytic reduction of 4-NTP.

COLL 34

Thermogel nanocomposites designed for biofilm disruption

Anna S. Samia, *anna.samia@case.edu*. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, United States

Bacterial biofilms are highly antibiotic resistant microbial cell associations that lead to chronic infections. Unlike planktonic bacterial cells, the biofilms are encapsulated in a hardly penetrable extracellular polymeric matrix that protects the pathogen from both the host immune response and antibiotics, and thus, demand innovative approaches for treatment. Recent advancements on the development of gel-nanocomposite systems with tailored therapeutic properties provide promising routes to develop novel antimicrobial agents that can be used to disrupt and completely eradicate pre-formed biofilms. In this talk, we will present our work on the development of novel a thermoresponsive hydrogel nanocomposite system, containing D-amino acids (D-AAs) and engineered nanoparticles, which can be delivered and transforms from a solution to a gel state at physiological temperature for sustained release of D-AAs and light or magnetic field-actuated thermal treatment of targeted infection sites. The D-AAs in the nanocomposite are known to inhibit biofilm formation and also disrupt existing biofilms. In addition, loading the hydrogel nanocomposite with gold or magnetic nanoparticles allows for combination thermal treatment following light stimulation (photothermal therapy) or magnetic field actuation (magnetic hyperthermia treatment), respectively. Using this novel two-step approach to utilize an externally actuated hydrogel

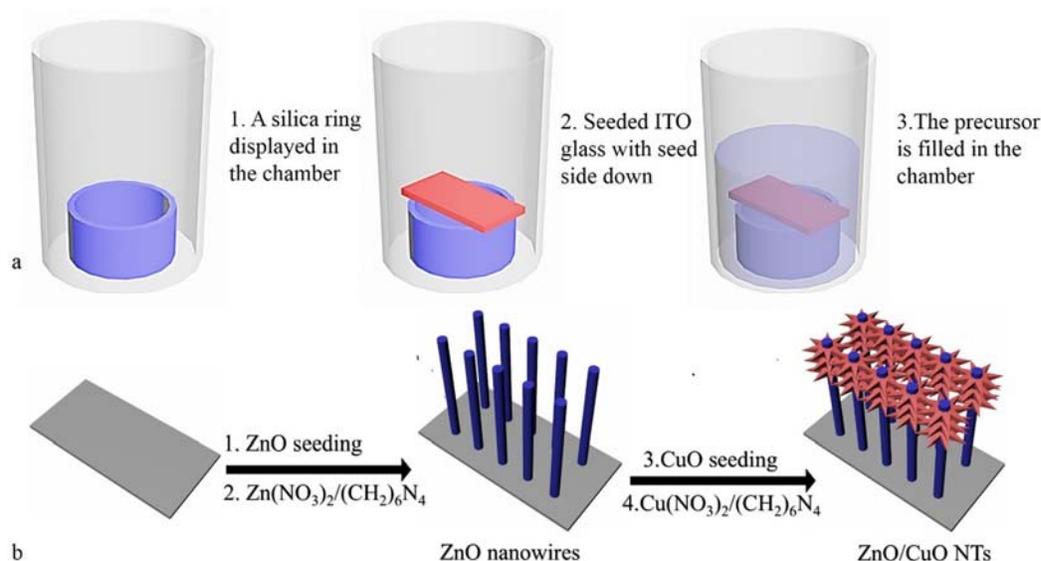
nanocomposite system for thermal treatment, following initial disruption with D-AAs, we were able to successfully demonstrate in cell studies the effective disruption and total eradication of *Staphylococcus aureus* biofilms, which were resistant to conventional antibiotics used in the clinic and were not completely cleared using individual D-AA or thermal treatments.

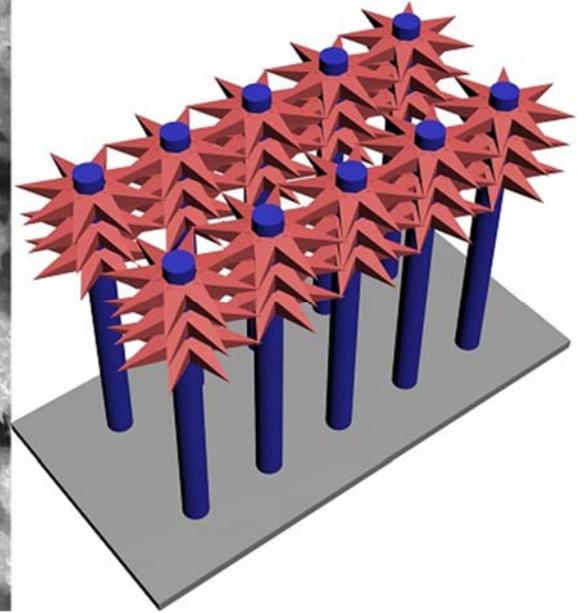
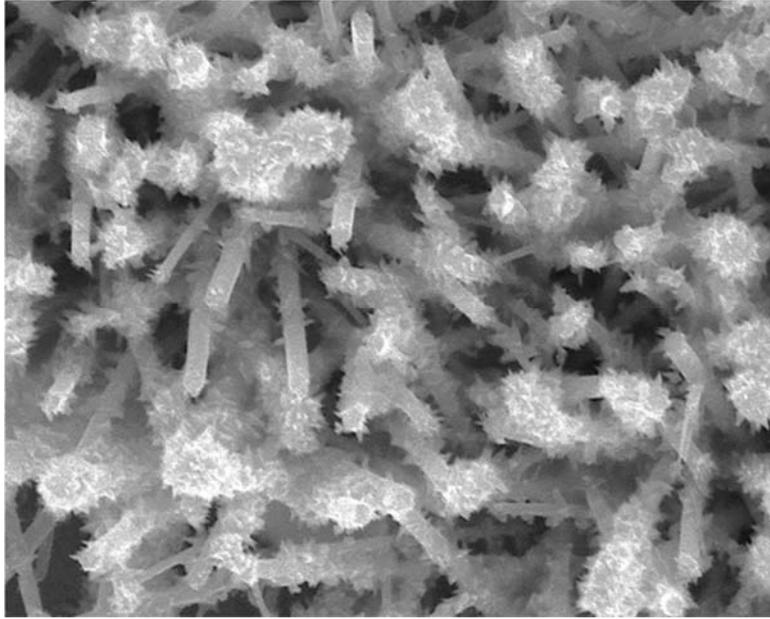
COLL 35

Fabrication of ZnO/CuO vertically-aligned tree-like nanostructure and its application in solar energy conversion

Zhengxin Li¹, *lizx@udel.edu*, **Meng Jia²**, **Baxter Abraham³**, **Jolie Blake¹**, **Daniel Bodine¹**, **John T. Newberg⁴**, **Lars Gundlach⁵**. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (3) Chemistry, University of Delaware, Merritt Island, Florida, United States (4) ISE Lab, Rm 456, University of Delaware, Newark, Delaware, United States (5) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States

Vertically aligned tree-like structures with n-type ZnO stems and p-type CuO branches were synthesized on indium tin oxide-coated glass via a simple seed-mediated hydrothermal technique. The nanotree structure features the p–n heterojunction at the branch/stem interface that facilitates charge separation upon illumination. The enhanced photocatalytic activity and light-energy conversion is determined via photoelectrochemical characterization under in aqueous and acetonitrile conditions, respectively. ZnO/CuO tree-like nanostructures are a prospective nanomaterial for the design of photoelectrochemical sensors, photocatalytic synthesis, and solar energy conversion.





COLL 36

Autoperforation of two-dimensional materials for generating colloidal electronic devices

Pingwei Liu^{2,1}, zjuliupingwei@gmail.com, **Albert Tianxiang Liu**³, **Daichi Kozawa**⁴, **Juyao Dong**⁵, **Volodymyr Koman**⁶, **Song Wang**¹, **Min Hao Wong**⁴, **Michael Strano**⁷. (1) Zhejiang University, Hangzhou, China (2) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (4) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (5) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (7) Chemical Engineering, 66-566, MIT, Cambridge, Massachusetts, United States

Graphene and other 2D materials possess desirable mechanical, electrical and chemical properties for incorporation into or onto novel colloidal particles, potentially granting them unique electronic functions. However, this application has not yet been realized because conventional top-down lithography scales poorly for the production of colloidal solutions. Due to its inherent stochasticity, brittle fracture is seldom used as a fabrication method for materials at the nanometer scale. However, Griffith theory allows for the imposition of a specific strain field that can guide fracture along a pre-set design. Herein, we show that this autoperforation provides a means of spontaneous assembly for surfaces comprised of 2D molecular surfaces without working at clean room. Chemical vapor deposited mono- and bi-layer graphene, molybdenum disulfide, or hexagonal boron nitride (hBN) can autoperforate into circular envelopes when sandwiching a microprinted spot assay of nanoparticle inks, allowing lift-off and assembly into solution. The resulting colloidal microparticles have two independently addressable, external Janus faces that we show can function as an intraparticle array of parallel, two terminal electronic devices. As an example, the printing of polystyrene

composite ink with 0.9 wt% black phosphorous results in micro-particles possessing non-volatile, 15 bit memory storage via a spatially addressable memristor array throughout the particle interior. The 2D envelopes demonstrate remarkable chemical stability for longer than 4 months of operation in aqueous buffer or even the highly acidic Human gastrointestinal environment and good mechanical stability in the aerosolization process. We further demonstrate that such particles form the basis of particulate electronic devices that can function as aerosolizable tattoo disks storing and transferring digital information, as well as dispersible and recoverable particulate electronics for large-scale collection of chemical information in water and soil.

COLL 37

Hierarchical porous SiC for efficient electromagnetic interference shielding at elevated temperatures

Zhijiang Wang, wangzhijiang@hit.edu.cn. Harbin Institute of Technology, Harbin Heilongjiang, China

High-efficiency electromagnetic interference (EMI) shielding materials are highly desired for practical shielding applications, especially in areas of aerospace and aircraft. Herein, a light but strong SiC foam with hierarchical porous architecture are fabricated by using dough or bread as raw material via carbonization and followed carbothermal reduction with silicon source. The fabricated SiC foam contains nano-, meso- and micro-sized porosities. Strikingly, meso and nano pores are embedded in micro-sized porous skeleton. This three-level hierarchical porous skeletons constitute the load-bearing structural units at gradually smaller length scales, which provides a means for dissipating strain. A significant synergistic among these hierarchical porous architecture endows the SiC foam with high-performance EMI shielding and thermal insulation. EMI shielding can be higher than 20 dB and specific EMI effectiveness exceeding 24.8 dB cm³ g⁻¹ in the frequency of 11 GHz at 25–600 °C, which is 3 times higher than dense SiC ceramic. The thermal conductivity reaches as low as 0.02 W m⁻¹ K⁻¹, which is comparable to aerogel. But the compressive strength is as high as 9.8 MPa. Considering the chemical and high-temperature stability of SiC, the fabricated SiC foam is a promising candidate for modern aircraft and automobile applications.

COLL 38

Oxidative dissolution and antimicrobial activity of silver nanoparticles: The role of particle dimensions, surface coating and shape

Qingbo Zhang, nanomaterialszh@gmail.com, Yue Hu, Vicki L. Colvin. Chemistry, Brown University, Providence, Rhode Island, United States

Silver nanoparticles are among the most extensively used nanomaterials in commercial products due to their antimicrobial properties. The oxidative dissolution of silver nanoparticles has significant influence on their biological properties since silver ions

released from the dissolution are largely responsible for their toxicity to microbes. The understanding of silver nanoparticle dissolution is not only of fundamental interest but also of great practical importance since this knowledge is crucial for optimizing antimicrobial performance in various applications as well as reducing their unintended environmental impact once released into ecosystem.

Here this dissolution process is studied as a function of particle dimension, shape, and surface chemistry using uniform silver nanoparticle libraries. It was found that the dissolution of silver nanoparticles is an equilibrium process. The equilibrium concentrations of silver ions are much lower than the values predicted from the thermodynamic calculation according to the oxidation reaction of silver. The low equilibrium concentration of silver ions is caused by the formation of a layer of oxidized silver on silver nanoparticle surface, which has a lower Gibbs energy than silver. Shape has the most profound influence on the extent of nanoparticle dissolution: triangular nanoprisms, for example, produced the highest equilibrium concentration of silver ions at the fastest rate. Surface coatings also can alter both the kinetics and extent of dissolution in a manner that depends sensitively on the coating surface density as opposed to its chemical composition. Finally, smaller nanoparticles both dissolve faster and yield higher equilibrium concentrations of silver ions. While this trend is expected because of the greater free energy of smaller nanocrystals, quantitatively the size dependence does not follow the anticipated Gibbs-Thompson relationship. This may reflect the complex surface composition of the nanocrystals whose oxidized surface structure is thought to depend on nanocrystal size. Both the thermodynamics and kinetics of the silver nanoparticle dissolution significantly influence their antibacterial properties.

These results illustrate how the material properties of silver nanocrystals may influence their dissolution property, and suggests strategies for optimizing antimicrobial properties as well as designing safer silver nanoparticles.

COLL 39

Ultra-thin zirconium hydroxide films: Characterization of material properties and assessment of chemical activity for chemical warfare simulant decomposition

Seokmin Jeon¹, *seokmin.jeon.ctr.ks@nrl.navy.mil*, **Robert B. Balow**², **Grant C. Daniels**³, *grant.daniels@nrl.navy.mil*, **Pehr E. Pehrsson**⁴. (1) National Research Council Research Associateship Program, Washington, District of Columbia, United States (3) Chemistry Division, U.S. Naval Research Laboratory, Washington, District of Columbia, United States

Amorphous zirconium hydroxide is a promising material to sorb and decompose environmentally toxic chemicals due to its high concentration of Lewis-acid and -base sites, including under-coordinated Zr defects and surface hydroxyl species. Commercially available powders are typically prepared by the sol-gel method, in which Zr salts are hydrolyzed in an acid or base solution. However, the resulting powdery

product has low adhesion and a large particle size distribution, which makes it unsuitable for thin, uniform, coatings on solid-state platforms. Electrochemically synthesized material, by contrast, can form conformal films on arbitrarily shaped electrodes, with nanometer-scale control of thickness, porosity, and morphology. While electrochemically synthesized zirconium hydroxide is an intermediate product in the production of ZrO₂ films, its physicochemical properties are poorly understood, despite their clear application for toxic chemical decontamination.

Here, we electrochemically synthesize zirconium hydroxide films and characterize them with X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, atomic force microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. Electrochemically synthesized zirconium hydroxide forms intact, monolithic films of <100 nm thickness on various conducting substrates, such as nanoparticle-decorated or nano-patterned surfaces, with controllable geometric parameters and chemical composition. Otherwise, it has virtually identical material properties to commercial powder. We assess the film's detoxification activity against a chemical warfare simulant, dimethyl methylphosphonate (DMMP), using attenuated total reflectance Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry.

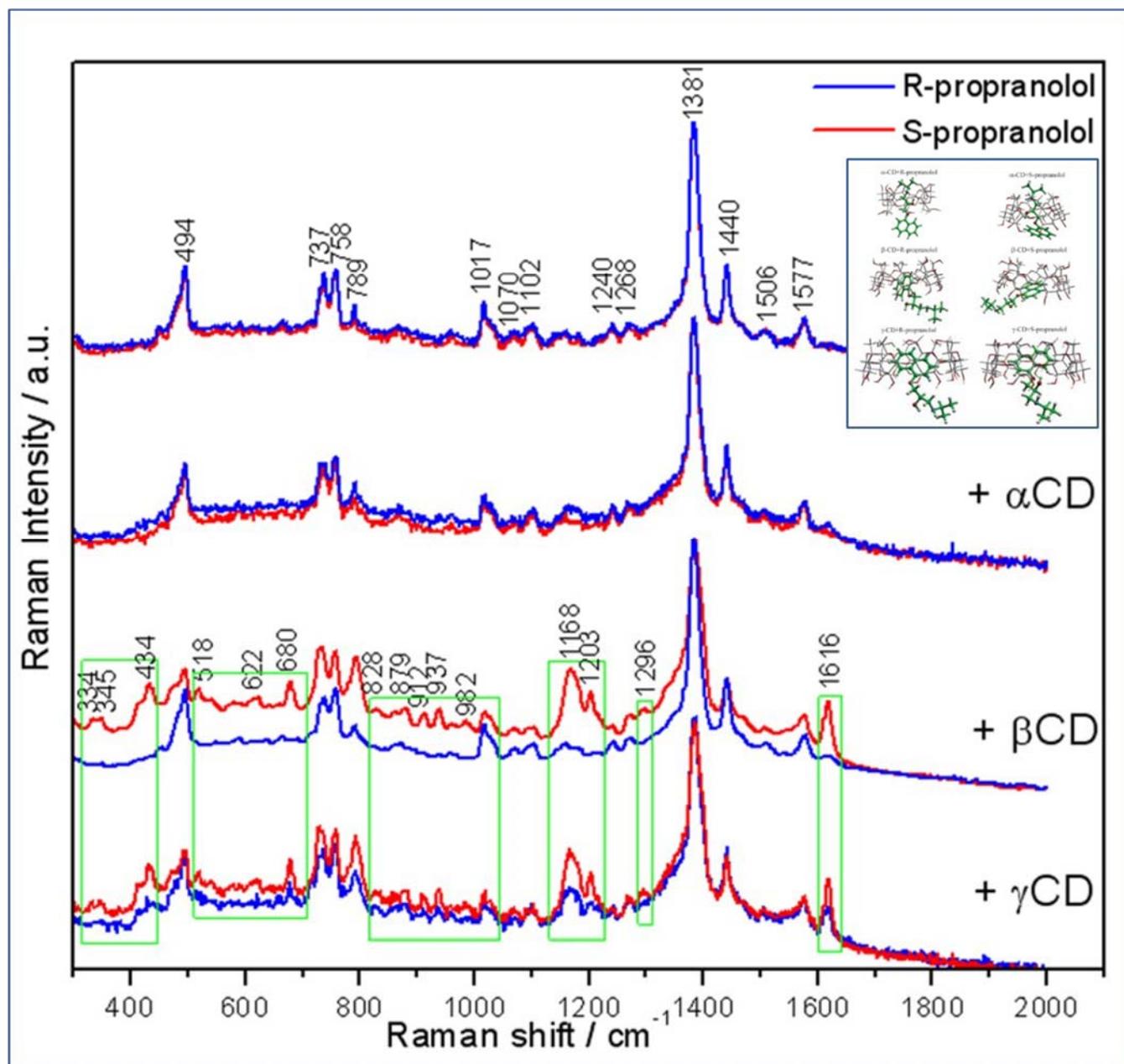
COLL 40

Nanoparticles mediated chiral separation using SERS

Rares Stiufiuc^{1,2}, rares.stiufiuc@umfcluj.ro, **Valentin Toma**², **Alin Moldovan**², **Gabriela Stiufiuc**³, **Vasile Chis**⁴, **Mihai Lucaciu**¹. (1) Faculty of Pharmacy, University of Medicine and Pharmacy, Cluj-Napoca, Cluj-Napoca, Cluj, Romania (2) MedFuture Research Center for Advanced Medicine, "Iuliu Hatieganu" University of Medicine and Pharmacy, Cluj-Napoca, Romania, Cluj-Napoca, Romania (3) Faculty of Physics, "Babes-Bolyai" University, Cluj Napoca, Romania (4) Faculty of Physics, "Babes-Bolyai" University, Cluj-Napoca, Romania

A very rapid, simple and reproducible SERS based approach for highly sensitive detection of chiral interactions between atenolol enantiomers and an achiral selector (cucurbituril) is presented. In a previous paper we have demonstrated the ability of SERS to qualitatively and quantitatively discriminate the two propranolol enantiomers based on their interactions with α , β and γ cyclodextrins. The different interactions of R and S propranolol with the three classes of CDs have been elucidated based on DFT calculations and SERS experiments. Here we push forward the limits of ultrasensitive SERS detection and demonstrate its capability to discriminate atenolol enantiomers using an achiral selector (cucurbituril [7]). The key component of this set up is represented by the solid SERS substrate, composed of gold nanoparticles self-assembled on a heated CaF₂ support. The monodispersed gold nanoparticles have been produced using an original microwave assisted synthesis method leading to the formation of spherical gold nanoparticles with a mean diameter of 13 nm. The nanoparticles self-assembling has been performed on an CaF₂ substrate heated at 50 degrees by pouring a very small volume of colloidal solutions onto the heated substrate. The highly efficient chiral recognition mechanism is based on synergistic interactions

between cucurbituril and the two atenolol enantiomers on one side and atenolol-cucurbituril complexes interactions with the nano substrate on the other side. The viability of this new SERS based method for chiral discrimination has been demonstrated for a molecule that has a very low Raman cross section, thus opening new perspectives for low cost chiral discrimination of a wide range of pharmaceutical compounds. The key role played by the nanosubstrate in the discrimination process is also investigated.



SERS spectra of R- and S-propranolol and of their supramolecular complexes with α -, β -, and γ -CDs.

COLL 41

Enantiomeric separations of chiral propranolol using chiral tetrahedral Au nanoparticles

Nisha Shukla¹, *nisha@andrew.cmu.edu*, **Darwin Yang**², **Andrew J. Gellman**². (1) *Institute of Complex Engineered Systems, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States* (2) *Department of Chemical Engineering, Carnegie Mellon Univ, Pittsburgh, Pennsylvania, United States*

Tetrahedral (THH, 24-sided) Au nanoparticles modified with D- or L-cysteine (Cys) have been used as enantioselective separators of the chiral pharmaceutical propranolol (PLL, used for anxiety and high blood pressure) in solution phase. Polarimetry has been used to measure the rotation of linearly polarized light by solutions containing mixtures of PLL and Cys/THH–Au NPs with varying enantiomeric excesses of each. Polarimetry yields clear evidence of enantiospecific adsorption of PLL onto the Cys/THH–Au NPs. This extends prior work using propylene oxide as a test chiral probe, by using the crystalline THH Au NPs with well-defined facets to separate a real pharmaceutical. This work suggests that chiral nanoparticles, coupled with a density separation method such as centrifugation, could be used for enantiomeric purification of real pharmaceuticals. A simple robust quantitative model has been developed to extract the enantiospecific equilibrium constants for R- and S-PLL adsorption onto the D- and L-Cys/THH–Au NPs. The model obviates the need for experimental determination of the surface area of absorbent Au nanoparticles which is extremely difficult to measure.

COLL 42

Substrate adhesion force scales non-monotonically with growth time in millimeter-scale carbon nanotube arrays

Ashley L. Kaiser¹, *kaisera@mit.edu*, **Dale L. Rautenbach**³, **Sophie C. Peterson**², **Luiz Acauan**³, **Stephen Steiner**³, **Roberto Guzman de Villoria**³, **Itai Y. Stein**², **Brian L. Wardle**³. (1) *Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States* (2) *Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States* (3) *Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States*

The excellent intrinsic and scale-dependent properties of aligned nanofibers, such as carbon nanotubes (CNTs) and their ability to be easily formed into multifunctional 3D architectures motivate their use as shape-engineerable materials. While controlling the nanofiber adhesion to the growth substrate is essential for this bulk-scale manufacturing and application-specific performance, limited experimental approaches and predictive models to date have neglected to address the scaling of CNT-substrate adhesion with CNT growth time, a crucial process parameter governing synthesis, structure, and properties. In this report, the non-monotonic scaling of the CNT-substrate adhesion

force with growth time is quantified and modeled based on the atomic and meso-scale evolution of the CNT, catalyst, and substrate interfaces. A novel experimental technique is developed to measure adhesion via uniform CNT array delamination from a flat growth substrate. Morphological and structural evolution is analyzed via scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. Modeling indicates an order of magnitude increase in adhesion after CNT growth termination, marking the transition between two distinct scaling regimes. Additionally, the observed increase in CNT wall thickness, sp^3 bond character, and reduced CNT number density with growth time shows that the accumulation of carbon species in the CNT array governs the mechanical response. These results provide insight into the elusive CNT growth termination process by linking this mechanism with the interfacial interactions responsible for achieving variable adhesion. Using this approach, the tunable substrate adhesion of aligned nanofibers may be realized, allowing for the design and manufacture of shape-engineerable materials applicable to consumer electronics, biomedical devices, and emerging nanoscale technologies.

COLL 43

Simple bond-centric model for accelerated nanoalloy energetics

Michael G. Taylor, mgt16@pitt.edu, Zihao Yan, Ashely Mascareno, Giannis Mpourmpakis. Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

Metal nanoparticles are finding tremendous applications in a broad range of modern technologies. However, understanding of nanoparticle stability as related to morphology (size/shape) and chemical ordering (e.g. in nanoalloys) remains somewhat limited. Toward understanding nanoparticle stability, first principles methods such as Density Functional Theory (DFT) are widely used and known to be accurate, but are limited to small nanoparticle sizes (<2nm in diameter) due to their high computational cost. Here, we developed a new bond-centric (BC) model that captures both cohesive energy trends over a range of mono- and bi-metallic nanoparticles along with mixing behavior (excess energy), in great agreement with DFT calculations. We apply our new BC model to evaluate the energetics of a recently reported 23,196-atom FePt nanoalloy to gain insights into both segregation and bulk chemical ordering behavior. Since our developed BC model utilizes only tabulated data (diatomic bond energies and bulk cohesive energies) along with readily-determined structural information of nanoparticles (coordination numbers), it is applicable to screen energetics of (almost) any nanoparticle morphology and chemical composition. Thus, this work holds the potential to significantly accelerate nanoalloy design.

COLL 44

Experimental validation of FM-AFM competition in $Fe_xZn_{1-x}Se$ QDs by computational modelling

Jasleen k. Bindra^{1,2}, jbindra@chem.fsu.edu, Lavrenty Gutsev¹, Geoffrey F. Strouse¹, Johan van Tol², Nar S. Dalal¹, Sebastain Stoian². (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States (2) Maglab, Florida State University, Tallahassee, Florida, United States

The onset of spin frustration with increasing iron incorporation into wurtzite ZnSe is computationally predicted and experimentally tested. Density functional theory (DFT) models indicate magnetic spin frustration arises due to formation of local Fe-Fe spin lattices within the ZnSe lattice. Comparison of the DFT-GGA spin models to the experimentally prepared 1.8 nm Fe_{0.1}Zn_{0.9}Se QD reveal the predicted spin frustration within the QD is observed by comparison to field and temperature dependent Mossbauer and magnetic susceptibility measurements. The use of computational methods that can anticipate the onset of desirable properties a priori in QDs prior to the synthetic preparation will enhance the toolset of the experimentalist when searching for specific magnetic properties.

COLL 45

Gold nanoparticles and biology: A perspective

Raphael Levy, rapha@liverpool.ac.uk. University of Liverpool, Liverpool, United Kingdom

Whilst nanotechnology and nanomedicine are generally seen as hot – even sometimes "revolutionary" - topics, gold nanoparticles have in fact been used in biology for therapeutic, diagnostic and biological research for over a hundred years. In this lecture, I will build from this historical context and from recent controversies on the structure (Stripy nanoparticles) and intracellular delivery of nanoparticles (SmartFlare/Spherical Nucleic Acids) to discuss some of the current challenges and opportunities in this field, illustrated by our work on the structure of peptide-capped gold nanoparticles and on the application of gold nanorods for in vivo cell tracking.

COLL 46

Engineering cellular interactions with nanolayered particles for controlled trafficking and delivery

Paula T. Hammond^{1,2}, hammond@mit.edu. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Koch Institute of Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Layer-by-layer assembly can provide a unique platform for the delivery of single drugs and synergistic drug combinations, and its use with drug-loaded core particles enables the co-encapsulation of DNA-damaging drugs, proteins and cytokines or other cytotoxic therapeutics with siRNA or other inhibitory drugs. The use of a simple, alternating

electrostatic assembly method to coat nanoparticles with polyelectrolyte assemblies can also lead to unique and dynamic outer surface layers that provide long blood half-lives, and exhibit an isoelectric point at physiologically relevant pH conditions to modulate nanoparticle uptake in hypoxic or inflamed tissues. Furthermore, simple assembled bilayers exhibit different modes of cellular trafficking based on the chemical composition and molecular structure of the final adsorbed layer. We have found that certain negatively charged polysaccharides and synthetic polypeptides can direct particles toward rapid intracellular uptake, slow caveolar uptake or extended membrane bound status without endosomal uptake in their engagement with ovarian cancer cells. Furthermore, we can use these interactions to derive new strategies for targeted delivery of different therapeutics, ranging from cytotoxic or silencing treatments to immuno-oncological approaches.

COLL 47

Nanomachines biointerfacing via cell membrane cloaking for active delivery and removal

Liangfang Zhang, zhang@ucsd.edu. Nanoengineering, MC-0448, University of California San Diego, La Jolla, California, United States

Nanoscale machines that can effectively convert diverse energy sources into movement and forces represent a rapidly emerging and fascinating robotic research area. Recent advances in the design, fabrication, and operation of nanomachines have greatly enhanced their power, function, and versatility. The new capabilities of these tiny untethered machines indicate immense potential for a variety of biomedical applications. In this talk the preparation and functional test of nanodevices enclosed in the plasma membrane of natural human cells are reported. The resulting biomimetic nanomachines are demonstrated to possess many surface functions of natural cells via studies of interactions with plasma proteins, cells, tissues, and microorganisms. The robust biological function and locomotion capacity of these cell membrane-cloaked nanomachines enable active delivery of payloads and efficient isolation of numerous biological threats.

COLL 48

Improving intracellular RNA delivery through nanocarrier design

Emily S. Day, emilyday@udel.edu. Biomedical Engineering, University of Delaware, Newark, Delaware, United States

Regulating gene expression through the intracellular delivery of small interfering RNA (siRNA) holds great promise as a strategy to study and treat cancer. Unfortunately, naked nucleic acids display limited cell uptake because of their high molecular weight and negative charge, and those that are internalized are at risk of degradation in endosomal and lysosomal compartments or by cytosolic enzymes. Researchers have

developed various nanocarriers to shuttle siRNAs into cells and protect them from premature degradation, but clinical translation of these carriers has been slow because there is limited knowledge regarding the parameters that dictate their biological interactions. We have developed two different types of siRNA nanocarriers and performed detailed studies to elucidate the mechanisms by which they operate inside cells. First I will discuss our work with polyethylenimine-coated spherical nucleic acids (PEI-SNAs), in which PEI is wrapped around a spherical nucleic acid core containing radially oriented siRNA. We have demonstrated that these PEI-SNAs undergo enhanced and more rapid cellular uptake than randomly assembled PEI-siRNA polyplexes, exhibit decreased lysosomal accumulation, enable more potent gene knockdown, and are more cytocompatible. These findings demonstrate that nanocarrier architecture plays a critical role in gene silencing efficiency. Second, I will discuss our work developing nanoshell-siRNA conjugates for temporal control over gene regulation. These nanocarriers keep their nucleic acid cargo inactive until it is released on-demand by externally applied pulsed near-infrared light, which is desirable because it prevents unintended widespread gene regulation. We have extensively characterized the mechanisms of siRNA release from nanoshells upon pulsed irradiation, and we have also shown that light-triggered gene silencing mediated by siRNA-nanoshell conjugates is considerably more potent than using commercial transfection agents to deliver siRNA into cells. Overall, our findings indicate the importance of thoroughly characterizing the biological interactions of RNA nanocarriers for applications in therapeutic gene regulation.

COLL 49

Size-dependent delivery of nanoparticles to brain assisted by focused ultrasound-mediated BBB disruption

Seiichi Ohta¹, s-ohta@m.u-tokyo.ac.jp, **Emi Kikuchi**², **Ayumu Ishijima**³, **Etsuko Kobayashi**³, **Takashi Azuma**^{1,2}, **Ichiro Sakuma**^{3,2}, **Taichi Ito**^{1,2}. (1) Center for Disease Biology and Integrative Medicine, The University of Tokyo, Tokyo, Japan (2) Department of Bioengineering, The University of Tokyo, Tokyo, Japan (3) Department of Precision Engineering, The University of Tokyo, Tokyo, Japan

Introduction:

Blood-brain barrier (BBB) hamper the delivery of drug carriers into brain. Recently, focused ultrasound (FUS) has been recognized as an emerging technique to overcome BBB. With the combination with microbubbles, FUS transiently opens gaps in BBB to enhance small drug permeation. For applying this technique for nanoparticle delivery, an important question is how large the opened BBB gaps are, and how long these gaps last. In this study, FUS-assisted BBB permeation of gold nanoparticles (AuNPs) with different size are examined *in vitro* and *in vivo* for elucidating the optimum design of NPs for brain drug delivery.

Materials and Methods:

3, 15, and 120 nm AuNPs were applied to bEnd3 cells cultured on Transwell® *in vitro*, and ICR mice via i.v. injection *in vivo* under existence of Sonazoid® microbubbles,

followed by FUS irradiation. TEER was measured to evaluate the barrier function of the *in vitro* BBB model. The amount of permeated AuNPs was measured using ICP-MS.

Results and discussion:

TEER measurement indicated that gaps are transiently opened for 4 h in the *in vitro* BBB model by FUS. The amount of permeated AuNPs *in vitro* was significantly increased by FUS for 3 and 15 nm NPs, while no significant difference was observed for 120 nm NPs. The permeated amount increased with decreasing NP size. FUS irradiation also significantly increased the NP delivery efficiency to brain *in vivo*. In the case of 0.7 MPa FUS, the efficiency increased by ca. 3-10 times. It was found that smaller NPs are not necessarily better, and 15 nm NPs showed the highest efficiency. We consider that this optimum size is determined by the competition between permeation through disrupted BBB gaps and blood half-life; while smaller NPs are better for the permeation through narrow gaps, they are rapidly excreted from blood by renal clearance. This hypothesis was supported by our kinetic model calculation that can express NP size-dependent permeation and clearance.

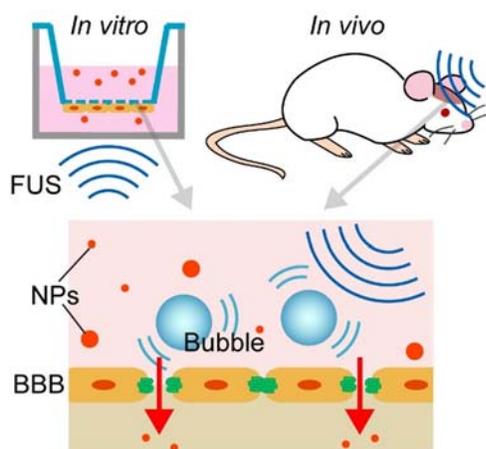


Fig. 1 Concept of this research

COLL 50

Site-selective and controlled immobilization of leptin on nanoparticles for improving cellular uptake

Vito Maggi^{1,2}, vito.maggi@iit.it, Vincenzo Mangini¹, Alberta Trianni^{1,3}, Francesca Melle^{1,3}, Roberto Fiammengo¹. (1) Center for Biomolecular Nanotechnologies@UniLe, Italian Institute of Technology - IIT, Arnesano, LE, Italy (2) Department of Engineering for Innovation, University of Salento, Lecce, LE, Italy (3) Department of Biological and Environmental Sciences and Technologies (DiSTeBA), University of Salento, Lecce, LE, Italy

The application of nanoparticles (NPs) as theranostic agents for brain disorders is hampered by the difficulty to overcome the blood–brain barrier (BBB). One possible strategy to tackle this problem is to target the NPs to a specific receptor localized at the

luminal side of the BBB and to take advantage of receptor-mediated transcytosis. In order to use this mechanism, leptin, a cytokine hormone, has been selected as our targeting ligand for conjugation to gold nanoparticles (AuNPs). We have chosen full length leptin instead of derivatized leptin peptides to fully exploit the protein targeting ability towards the cognate receptor and we have improved NP targeting performances by controlling the leptin orientation with a site-selective derivatization strategy. This non-conventional approach is based on the disulfide rebridging in the presence of a dithiophenolmaleimide linker and was compared with a more common non-site-selective protein derivatization strategy. Finally, the derivatized-leptins were conjugated to PEGylated-AuNPs via "click chemistry" reactions. In this contribution, we discuss the molecular design, the preparation and characterization of these NPs. We confirm leptin conjugation by amino acid and dot-blot analysis. Moreover, we test the efficacy of leptin-conjugated AuNPs *in vitro* on MCF-7 cells. The site-selective leptin conjugated NPs are internalized by MCF-7 cells 5 times more efficiently than the non-site-selective ones, as proved by using ICP-OES and CLM. We also demonstrated the transport of leptin-AuNPs across an *in vitro* BBB model (hCMEC/D3 cells). In conclusion, this is the first example of site-selective conjugating full length leptin to inorganic NPs and paves the way to novel perspectives in nanomedicine for instance for the development of theranostic tools for brain diseases.

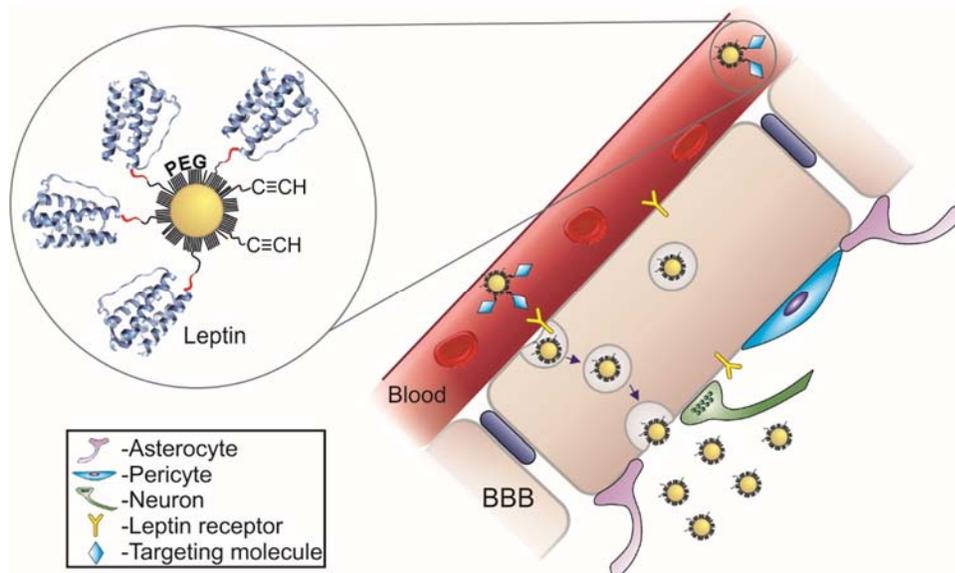


Figure 1. Schematic representation of Leptin-AuNPs transcytosis across the BBB.

COLL 51

Heterocellular 3D platforms and *in vivo* dual-nanotracer molecular imaging provide clinically-relevant insights to facilitate the development of antibody-targeted, NIR-active nanotherapeutics

Girgis Obaid¹, Obaid.Girgis@mgh.harvard.edu, **Shazia Bano**¹, **Kimberly Samkoe**², **Srivalleesha Mallidi**¹, **Jerrin Kuriakose**¹, **Brian Pogue**², **Tayyaba Hasan**¹. (1) Wellman Center for Photomedicine, Massachusetts General Hospital and Harvard Medical School, Boston, Massachusetts, United States (2) Geisel School of Medicine, Dartmouth College, Hanover, New Hampshire, United States

Two challenges that face the successful development of antibody-targeted NIR-active nanotherapeutics (ATNs) include the synthetic complexity of nanofabrication and the lack of clinically relevant screening approaches to rapidly verify their tumor specificity. Using a modular synthetic approach, we fine-tuned ATNs directed towards the tumor-associated biomarker, epidermal growth factor receptor (EGFR), using the FDA approved antibody cetuximab. In a high-throughput 3D heterocellular model of pancreatic cancer that contains patient-derived fibroblasts, we showed that the ATNs efficiently penetrate the tumor tissue in under 1 hour whilst maintaining up to 8-fold specificities towards tumor cells. This translated to an impressive 16-fold improvement in targeted phototoxicity of the heterocellular 3D nodules, as compared to no targeting. Edging further towards *in vivo* success, we harnessed a powerful paired-nanotracer molecular imaging approach to establish that our ATNs successfully engage with EGFR-positive tumors *in vivo*. Importantly, we showed that the receptor concentrations available for ATN binding *in vivo* closely resemble those available for the natural ligand, EGF, making the nanotherapeutic a viable candidate for targeted *in vivo* treatment. The systematic approach we outline here serves as a rational workflow for designing, engineering and evaluating complex, multi-agent antibody directed nanotherapeutics to minimize failure, and expedite the translation of less toxic and more efficacious targeted nanomedicines into the clinical arena.

COLL 52

Investigating the *in vitro/in vivo* disconnect using gold nanoparticles

Jacob M. Berlin, jberlin@coh.org. Molecular Medicine, Beckman Research Institute at City of Hope, Duarte, California, United States

The field of nanomedicine has received much attention for its potential to allow for targeted identification and treatment of tumors, while sparing healthy tissue. This promise has yet to be clinically realized; instead nanomedicine has translated into clinical benefit via formulations that improve the pharmacokinetics and toxicity profiles of toxic chemotherapeutic agents. It is well recognized that clearance by the mononuclear phagocytic system (MPS), particularly the liver, is the primary challenge to achieving tumor targeted delivery. However, it remains unclear exactly what drives liver accumulation. Kupffer cells have been repeatedly identified as liver cells that uptake nanoparticles and there has been work focused on developing nanoparticles that avoid macrophage uptake in order to thus avoid liver clearance. We have recently shown that small molecule coatings on metallic nanoparticles can markedly reduce *in vitro* cell uptake for very sparsely PEGylated nanoparticles. Similar results were obtained in media with and without proteins, suggesting that protein

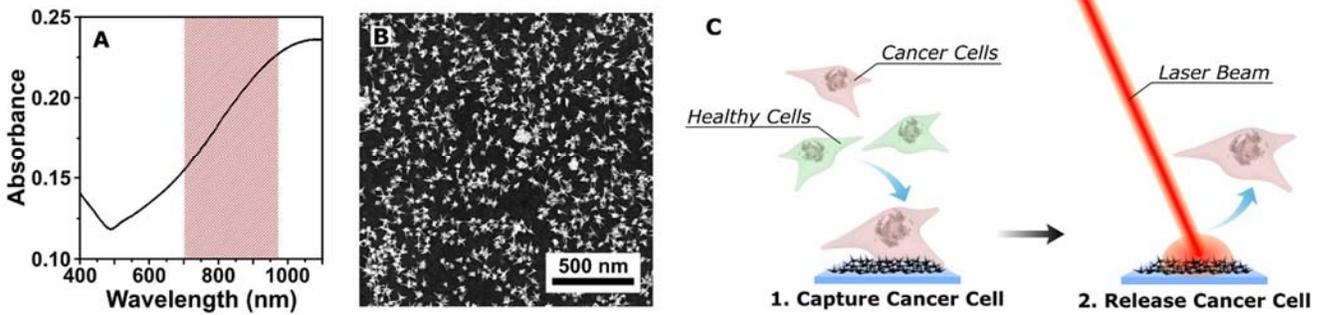
opsonization is not the primary driver of this phenomenon. However, in vivo, these materials robustly accumulate in the liver (and other MPS organs) highlighting an in vitro/in vivo disconnect common to many nanoparticles. We have now conducted detailed studies of liver uptake of these and related materials and present a model to reconcile the results.

COLL 53

Gold nanospikes enable capture and release of circulating tumor cells

Leonardo Scarabelli^{2,1}, scarabelli.leonardo@gmail.com, Gail A. Vinnacombe^{2,1}, Liv K. Heidenreich^{2,1}, Naihao Chiang^{2,1}, Steven J. Jonas^{3,4}, Paul S. Weiss^{1,2}. (1) California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California, United States (2) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States (3) Eli & Edythe Broad Center of Regenerative Medicine and Stem Cell Research, University of California, Los Angeles, Los Angeles, California, United States (4) Children's Discovery and Innovation Institute, University of California, Los Angeles, Los Angeles, California, United States

Development of new strategies for diagnosing and monitoring cancer in its early stages are key steps towards more efficient anticancer therapies. Circulating tumor cells (CTCs), malignant cells that break away from primary metastatic lesions, have been proposed as “liquid biopsies”, able to provide real-time information about a patient’s disease status. Improvements in technologies for the screening and collection of CTCs can enable a broad range of clinical applications, including early detection of disease and discovery of new biomarkers to predict treatment responses and disease progression. We are developing and applying a microfluidic platform integrated with nanostructured branched plasmonic interfaces to enable selective capture and recollection of CTCs. Gold nanostars are grown *in situ* on the interior walls of a glass capillary using a fast and scalable synthetic protocol and are chemically modified with specific antibodies to enable the selective capture of Ewing Sarcoma cells. These nanostructures are characterized by strong plasmonic responses in the near infrared and nanometer tip curvatures that enable efficient photon-to-heat conversion through plasmon-phonon coupling (**Figure A** and **B**). This localized hyperthermia effect has been applied for the controlled “soft” detachment of adherent cells, and coupled to our platform and will enable the concentration and collection of captured CTCs for further analysis (**Figure C**). We aim to develop devices capable of high-throughput detection and isolation of CTCs, enabling early sensing of cells with metastatic potential for monitoring disease.



COLL 54

Ultrasmall core-shell silica nanoparticles as targeted imaging probes for cancer nanomedicine: Design, evaluation and clinical translation

Michelle Bradbury, bradburm@mskcc.org. Radiology, Memorial Sloan Kettering Cancer Center, New York, New York, United States

Despite recent advances in cancer-targeted imaging probe developments for nanomedicine, clinical translation remains challenging. Nanomaterials platforms currently under evaluation in oncology clinical trials are largely non-targeted drug delivery vehicles or devices to thermally treat tissue; these are typically not surface modified for targeted detection by clinical imaging tools. New tumor-selective platforms need to satisfy critical safety benchmarks, in addition to assaying targeted interactions with the microenvironment and their effects on biological systems. Coupled with metabolic imaging and analysis tools, such as PET, quantitatively accurate data sets for whole body distributions, targeting kinetics, and clearance profiles of new platforms transitioning into early-phase clinical trials can be acquired.

Advances in nanotechnology have also fueled a paradigm shift in targeting and safely delivering drugs in conjunction with image-directed approaches. The size, architecture, and chemical composition of particle-based drug delivery vehicles can be fine-tuned to achieve properties optimal for loading and controlled release of therapeutic agents, patient safety/compliance, favorable kinetic profiles, and reducing unwanted side effects. By combining therapeutic particle tracer preparations with quantitative bioimaging approaches, drug delivery, lesion localization, and the extraction of key tumor biologic properties can be achieved for individualizing treatment planning.

The ability to flexibly adapt the formulation of clinically-promising drugs to improve their physicochemical and/or biological properties, in combination with metabolic imaging tools, will be important to quantify and establish suitable clinical trial endpoints. Issues relating to solubility, transport, barrier penetration, time-dependent changes in drug uptake, and intratumoral distribution are additional considerations. These properties are often not generally evaluated in the context of drug delivery due to the complexity of the biological systems involved. The future success of molecular medicine will, in part, rest upon our ability to offer improved clinical trial designs addressing the foregoing issues. In conclusion, the adoption of such an approach for image-directed drug delivery in

clinical settings will have far-reaching implications for personalizing cancer care in terms of treatment planning, stratification to appropriate trial arms, and response monitoring.

COLL 55

Promoting intratumoral delivery, active targeting and clearance with sub-5 nm ultrafine magnetic iron oxide nanoparticles

Hui Mao, hmao@emory.edu. Department of Radiology and Imaging Sciences, Emory University School of Medicine, Atlanta, Georgia, United States

While major advances have been made in developing and engineering nanomaterials for in vivo applications of biomedical imaging and therapeutics delivery, major challenges in delivery efficiency, effective biomarker targeting, and appropriate control of the pharmacokinetics and clearance profiles remained to be further addressed. Here we present our strategy to these limitations by “going smaller” with 3 nm core-sized ultrafine iron oxide nanoparticles (uIONPs) developed in our lab. Using this sub-5 nm nanoparticle platform, a series of imaging experiments in vivo and ex vivo and quantitative image analysis, we demonstrate that the intratumoral delivery can be facilitated by exerting the extravasation of the nanoparticles from the tumor vasculature, one of the main factors in the enhanced permeability and retention (EPR) effect that is not fully utilized with larger sized nanoparticles. When surface functionalized with targeting ligands, such as transferrin (Tf) to target transferrin receptor (TfR) over expressed tumors, Tf-uIONP (3 nm core size) exhibited substantially improved active targeting with higher ratio of ligand-mediated targeted delivery vs. just EPR driven passively targeted delivery when comparing to the non-targeted uIONP and larger IONPs (30 nm core size) in a 4T1 breast cancer tumor model. These new findings not only support the rationale and value of pursuing ligand-mediated biomarker targeted delivery of nanoimaging probes and nanotherapeutics via active targeting, but also suggest the potential to improve biomarker quantification in vivo with imaging and quantitative monitoring of a targeted treatment in precision medicine. For future clinical translation, sub-5 nm uIONPs showed favorable pharmacokinetics profile for imaging and drug delivery and moderate renal clearance complementary to typical slow clearance and long retention time of large nanoparticles by the reticuloendothelial system (RES), which has been an increasing concern for in vivo applications of nanomaterials.

COLL 56

Noninvasive fluorescence kidney functional imaging enabled by renal clearable luminescent gold nanoparticles

Mengxiao Yu^{1,2}, mengxiaoyu.clearnanomed@gmail.com, Xuhui Ning³, Jing Xu², Bujie Du⁴, Jie Zheng⁵, Jiancheng Zhou⁶, Jer-Tsong Hsieh⁶, Payal Kapur^{7,6}. (1) ClearNano, Inc, Frisco, Texas, United States (2) Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States (3) Chemistry & Biochemistry,

University of Texas at Dallas, Richardson, Texas, United States (4) Chemistry & Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States (5) Chemistry, UT Dallas, Richardson, Texas, United States (6) Urology, The University of Texas Southwestern Medical Center, Dallas, Texas, United States (7) Pathology, The University of Texas Southwestern Medical Center, Dallas, Texas, United States

Kidney disease affects more than 10% of adults worldwide but is hardly detected at early stages with conventional renal function biomarkers. To improve the fundamental understanding of kidney disease, it is highly desired to develop a low-cost, high-sensitivity preclinical imaging technique that can not only identify kidney dysfunction at early stages but also differentiate between the stages of kidney dysfunction. As a low cost technique, *in vivo* fluorescence imaging has been widely used for studying many diseases such as cancer; however, noninvasive fluorescence imaging of kidney function is challenging due to low kidney-contrast enhancement of organic dyes. Here, we report that rapid and persistent accumulation of conventional dyes in the skin “shadowed” real fluorescence signals from the kidneys and prevented noninvasive imaging of kidney function, which can be addressed with renal clearable near infrared emitting gold nanoparticles. By integrating near infrared emission with efficient renal clearance and ultralow background interference, gold nanoparticles can increase kidney contrast enhancement by 50 fold over near-infrared fluorophore IRDye 800CW. Furthermore, noninvasive fluorescence kidney functional imaging, enabled by renal clearable near infrared emitting gold nanoparticles, can noninvasively detect kidney dysfunction, report on the dysfunctional stages, and even reveal adaptive function in a mouse model of unilateral obstructive nephropathy, which cannot be diagnosed with routine renal function markers. These results demonstrate that low cost fluorescence kidney functional imaging is highly sensitive and useful for the longitudinal, noninvasive monitoring of kidney dysfunction progression in preclinical research.

COLL 57

Treatment of bacterial infections with peptide-targeted porous silicon nanoparticles

Michael J. Sailor, *msailor@ucsd.edu*. UCSD Chemistry, La Jolla, California, United States

The use of porous Si nanoparticles for peptide-targeted delivery of siRNA and small molecule drugs to treat lethal bacterial infections in mice will be described. Porous Si nanoparticles can be simultaneously loaded and sealed using aqueous solutions of the desired therapeutic in the presence of calcium or magnesium ions. The resulting nanostructures consist of a drug-loaded porous silicon nanoparticle sealed with biodegradable calcium or magnesium silicate. The structures are then coated with lipids or poly(ethylene glycol) moieties to increase circulation time, and attachment of functional peptides to these coatings imparts targeting and cell penetration properties to the constructs. The targeted nanoparticles show improved gene silencing and therapeutic outcomes *in vivo*. The intrinsic photoluminescence that derives from

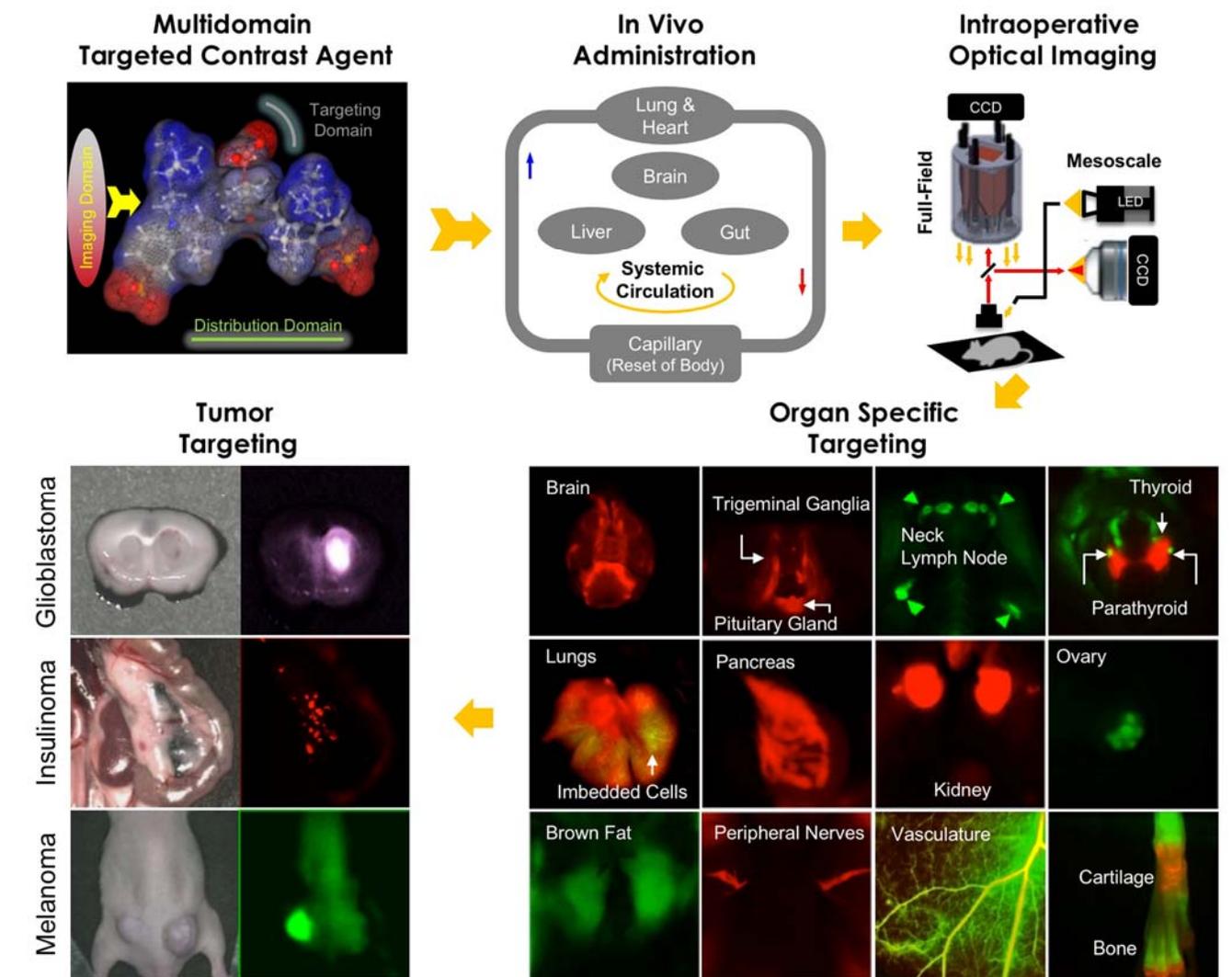
quantum confinement in the silicon skeleton provides a built-in luminescent probe that can be used to track the particles in vivo and to allow a self-reporting drug delivery feature.

COLL 58

Design considerations of contrast agents for bioimaging and nanomedicine

Hak Soo Choi¹, hchoi12@mgh.harvard.edu, **Homan Kang**². (1) Medicine, Harvard Medical School, Boston, Massachusetts, United States (2) Radiology, Massachusetts General Hospital, Charlestown, Massachusetts, United States

Two fundamental and unsolved problems facing bioimaging and nanomedicine are nonspecific uptake of intravenously administered diagnostic and/or therapeutic agents by normal tissues and organs, and incomplete elimination of unbound targeted agents from the body. To solve these problems, we have synthesized a series of indocyanine near-infrared (NIR) fluorophores that varied systematically in net charge, conformational shape, hydrophilicity/lipophilicity, and charge distribution. Using 3D molecular modeling and optical fluorescence imaging, we have defined the relationship among the key independent variables that dictate biodistribution and tissue-specific targeting such as lung and sentinel lymph nodes, human prostate cancers, and human melanomas. Recently, we have developed new pharmacophore design strategy “structure-inherent targeting,” where tissue- and/or organ-specific targeting is engineered directly into the non-resonant structure of a NIR fluorophore, thus creating the most compact possible optical contrast agent for bioimaging and nanomedicine. The biodistribution and targeting of these compounds vary with dependence on their unique physicochemical descriptors and cellular receptors, which permit 1) selective binding to the target tissue/organ, 2) visualization of the target specifically and selectively, and 3) provide curing options such as image-guided surgery or photo dynamic therapy. Our study solves two fundamental problems associated with bioimaging and nanomedicine and lays the foundation for additional targeted agents with optimal optical and *in vivo* performance.



COLL 59

Glomerular barrier behaves as an atomically precise bandpass filter in a sub-nanometre regime

Bujie Du, dubujie0129@gmail.com. Chemistry & Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States

The glomerular filtration barrier is known as a “size cut-off” slit, which retains nanoparticles or proteins larger than 6~8 nm in the body and rapidly excretes smaller ones through the kidneys. However, in the sub-nm size regime, we have found that this barrier behaves as an atomically precise “bandpass” filter to significantly slow down renal clearance of few-atom gold nanoclusters (AuNCs) with the same surface ligands but different sizes (Au₁₈, Au₁₅ and Au₁₀₋₁₁). Compared to Au₂₅ (~1.0 nm), just few-atom decreases in the size result in four- to ninefold reductions in renal clearance efficiency in the early elimination stage, because the smaller AuNCs are more readily trapped by the

glomerular glycocalyx than larger ones. The unique *in vivo* nano-bio interaction in the sub-nm regime also slows down the extravasation of sub-nm AuNCs from normal blood vessels and enhances their passive targeting to cancerous tissues through an enhanced permeability and retention effect. This discovery highlights the size precision in the body's response to nanoparticles and opens a new pathway to develop nanomedicines for many diseases associated with glycocalyx dysfunction.

COLL 60

Light, heat and sound to enhance nanoparticle delivery to the tumors

*Marta Overchuk^{1,2}, Carly Pellow^{1,2}, Danielle Charron^{1,2}, Kara Harmatys^{1,2}, Maneesha Rajora^{1,2}, Juan Chen², **Gang Zheng^{1,2}**, gang.zheng@uhnres.utoronto.ca. (1) University of Toronto, Toronto, Ontario, Canada (2) Princess Margaret Cancer Centre, Toronto, Ontario, Canada*

Drug encapsulation into a nanoparticle improves its pharmacokinetics, decreases its toxicity and enables co-delivery of multiple drugs with contrast agents. Despite being widely explored, this approach has not been proven more efficacious in cancer eradication compared to free chemotherapy drugs, primarily due to low nanoparticle tumor uptake and heterogenous intratumoral distribution. To overcome these hurdles, multiple pre-treatment strategies that improve tumor permeability have been proposed, including chemically-induced vasodilation, radiation therapy, vascular-targeted photodynamic therapy (PDT), focused ultrasound, and local hyperthermia.

Our lab has been exploring external means to enhance nanoparticle delivery to tumors via light, heat, and sound. First, we employed a low molecular weight (<2 kDa) porphyrin photosensitizer targeting prostate-specific membrane antigen (Porphy-PSMA) in combination with sub-lethal PDT to enhance delivery of 100 nm liposomes, 20 nm lipoproteins and 15 nm gold nanoparticles, as demonstrated by fluorescence/photoacoustic imaging and ICP-MS, respectively. We found that the low molecular weight of Porphy-PSMA allows it to homogeneously distribute within the tumor, and its combination with PDT opens access to the deep layers of the tumor tissue for nanoparticle delivery. Secondly, we used lipid-based nanoparticles containing highly ordered porphyrin J-aggregates to locally administer photo-hyperthermia to tumors. The ordered porphyrins act as self-regulating photothermal agents, which allowed us to maintain the tumour temperature below therapeutic doses to efficiently enhance subsequent nanoparticle tumor accumulation. Finally, following our recent discovery of ultrasound-induced microbubble-to-nanoparticle conversion, we explored a strategy to harness this conversion as a tool to bypass the enhanced permeability and retention effect in order to directly deliver nanomedicines into tumors.

Given the minimally invasive nature of these external triggers (light, heat, and sound), these new approaches could enhance both overall tumor accumulation and the intratumoral distribution of nanomedicines, which ultimately could lead to improvement in the therapeutic efficacy of FDA-approved nanoformulations.

COLL 61

***In vivo* transport of engineered nanoparticles in the kidneys**

Jie Zheng, *jxz087000@utdallas.edu. Chemistry, UT Dallas, Richardson, Texas, United States*

Fundamental understandings of how engineered nanoparticles are transported in the kidneys are importance of developing new medical technologies for early disease detection and treatment as well as expediting their clinical translation. In this talk, I will provide a brief summary of our current understandings of how engineered nanoparticles are transported in the kidneys and some potential applications derived from these understandings as well as future challenges in this field.

COLL 62

Tumor-targeted and clearable protein-based MRI nanoprobos

Yang Zhao^{1,2}, *mryangzhao@yahoo.com, Jing Peng*³, *Gang Han*⁴. (1) *University of Massachusetts- Medical School, Worcester, Massachusetts, United States* (2) *Radiology, The 2nd Hospital of Tianjin Medical University, Tianjin, Tianjin, China* (3) *The Second Hospital of Tianjin Medical University, Tianjin, China* (4) *Biochemistry and Molecular Pharmacology, University of Massachusetts-Medical school, Worcester, Massachusetts, United States*

Biocompatibility, targeting, and clearance are key challenges in the design of new MRI contrast agents. Herein, we report on a tumor-targeting, gadolinium biomineralized human transferrin (Tf) protein-based nanoparticle (Gd@Tf NP) for MRI use. As compared to the conventionally used gadolinium chelates, the resultant Gd@Tf NPs possess outstanding chemical stability and exhibited superior longitudinal relaxation. More importantly, our MR images show that Gd@Tf indeed retained the natural tumor targeting ability and the subsequent tumor retrieval biofunctions of Tf. Thus, such Tf protein-based MR NPs integrate T1 signal amplification, precise tumor targeting, and systematic clearance capabilities. They offer a new approach to design biocompatible multifunctional MRI contrast agents for a wide range of clinical imaging and treatment applications.

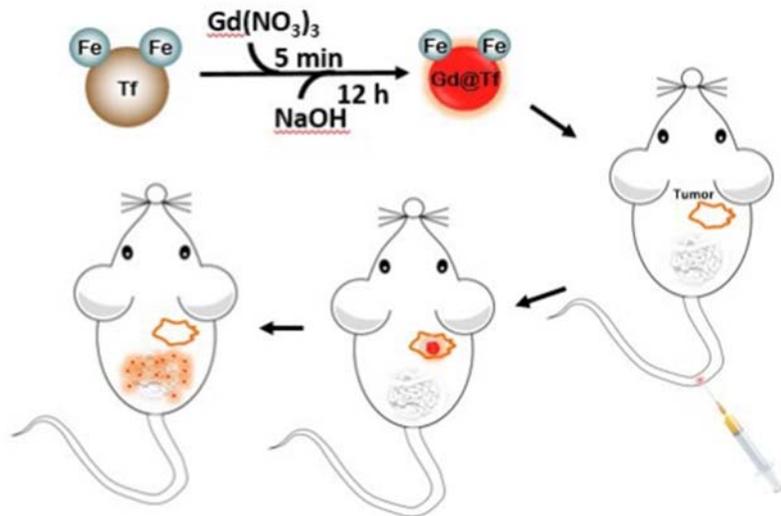


Figure 1. The Gd nanoparticles biomineralized in the template of Tf proteins. After tail vein injection, Gd@Tf NPs were accumulated in the tumor areas and finally eliminated from the body via the hepatobiliary system, which demonstrates that Gd@Tf NPs are tumor targeting and metabolically clearable.

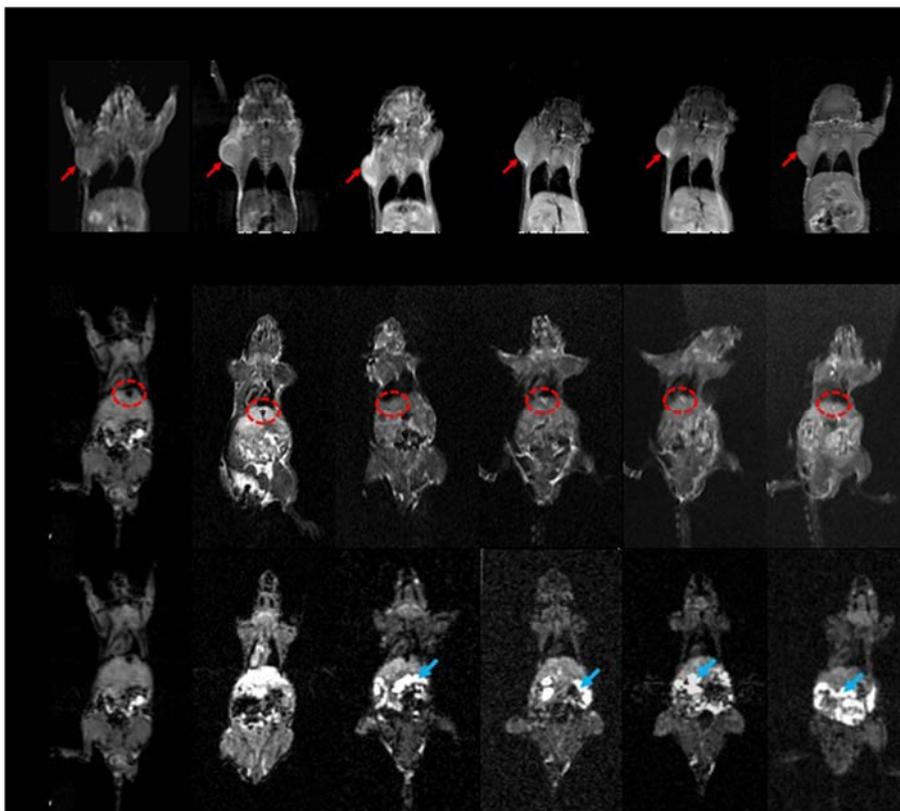


Figure 2. In-vivo T1-weighted MR images of PC-3 tumor-bearing mice after the intravenous injection of Gd@Tf NPs. (A) The targeted MR imaging of PC-3 tumors. (B) The dynamic MR

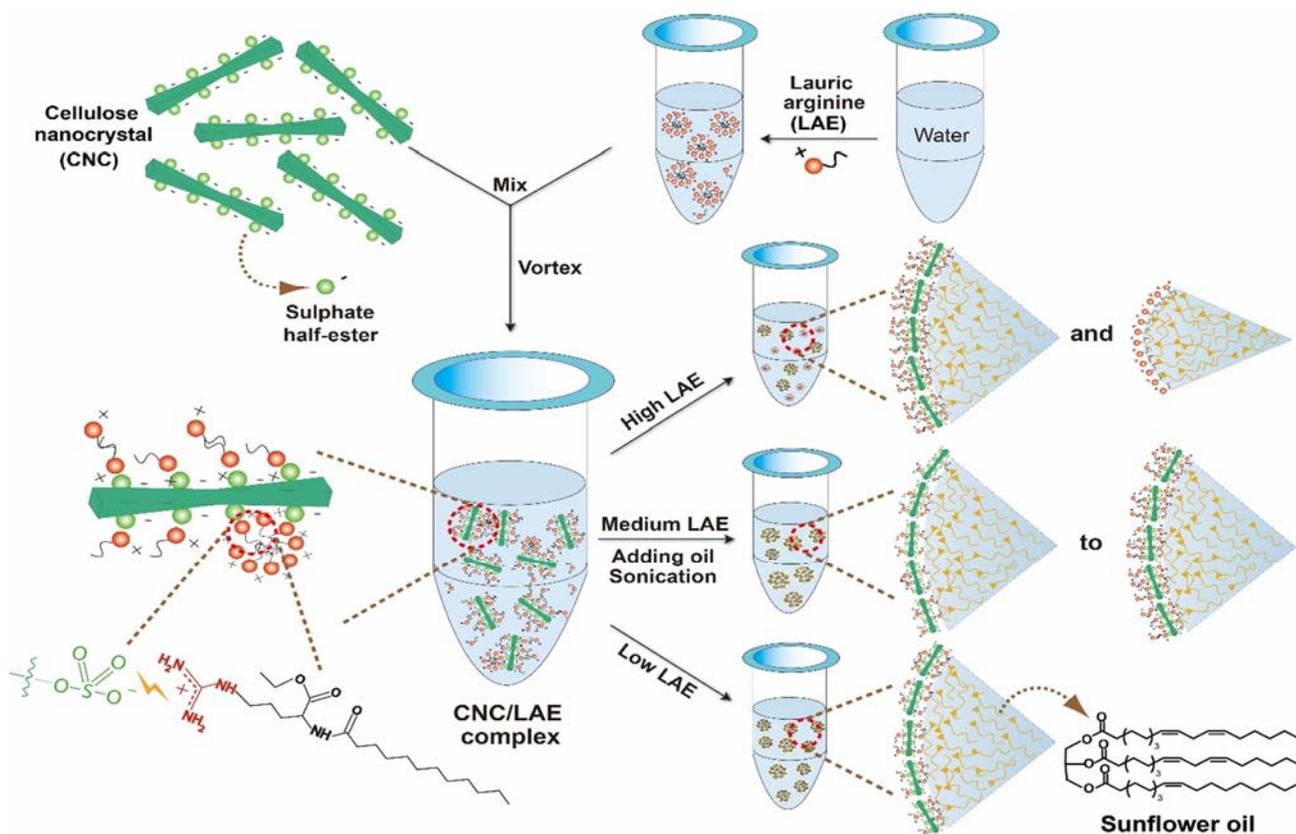
visualization of the Gd@Tf metabolism via the hepatobiliary system. Red circles: the the gall bladder, blue arrows: intestine.

COLL 63

Formulation and stabilization of concentrated edible oil-in-water emulsions based on electrostatic complexes of a food-grade cationic surfactant (ethyl lauroyl arginate) and cellulose nanocrystals

Long Bai, *longbai2011@hotmail.com*, *Wenchao Xiang*, *Siqi Huan*, *Orlando J. Rojas*. *Aalto University, Espoo, Finland*

We report on oil-in-water Pickering emulsions with high concentration of the oil phase that are stable against coalescence during storage. For this, viscous, edible oil (sunflower) was emulsified in the presence of naturally-derived cellulose nanocrystals (CNC) and a food-grade, bio-based cationic surfactant obtained from lauric acid and L-arginine (ethyl lauroyl arginate, LAE). The interactions between CNC and LAE were elucidated by isothermal titration calorimetry (ITC) and supplementary techniques. LAE adsorption on CNC surfaces and its effect on nanoparticle electrostatic stabilization, aggregation state, and emulsifying ability was studied and related to the properties of resultant oil-in-water emulsions. Pickering systems with tunable droplet diameter and stability against oil coalescence during long-term storage were controllably achieved depending on LAE loading levels. The underlying stabilization mechanism was found to depend on the type of complex formed, the LAE structures adsorbed on the cellulose nanoparticles (as unimer or as adsorbed admicelles), the presence of free LAE in the aqueous phase, and the equivalent alkane number of the oil phase (sunflower and dodecane oils were compared). Our results provide an example of an eco-friendly modification strategy for CNC by combining a food-grade cationic surfactant and a simple preparing protocol. The results extend the potential of CNC in the formulation of high-quality and edible Pickering emulsions. The functional properties imparted by LAE, a highly effective molecule against food pathogens and spoilage organisms, opens new opportunities in food, cosmetics, and pharmaceutical applications, where the presence of CNC plays a critical role in achieving synergistic effects with LAE.



Schematic illustration (not to scale) for preparation and stabilization of nanocellulose-based Pickering emulsions via electrostatic interactions involving CNC and LAE, representing a sustainable way to construct multiscale green materials

COLL 64

Rapid detection of foodborne pathogens using directional emission from dynamic double emulsion droplets

Lukas Zeininger, lukaszei@mit.edu, Timothy M. Swager. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Multiphase complex emulsions formed from two or more immiscible solvents offer a unique platform as new materials for chemical sensor applications. The temperature controlled miscibility of fluorocarbons (F) and hydrocarbons (H) enables a temperature induced phase-separation, leading to structured emulsion droplets of H and F in water (W), which can be alternated between encapsulated (F in H, and H in F), and Janus configurations by varying the interfacial tensions using surfactants. These complex emulsion droplets can selectively invert morphology in response to external stimuli such as the presence of specific analytes, small pH changes, light or high energy irradiation, and the presence of an electric or magnetic field. Here we will show how the addition of stimuli-responsive surfactants to one of the phases of the complex emulsions provides a

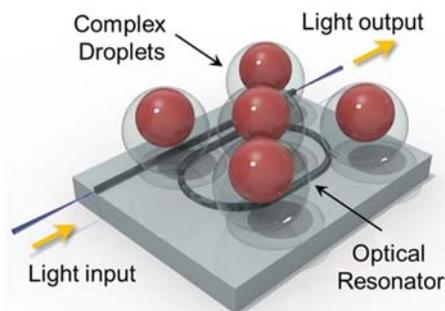
method to induce such a morphology change as a response to the presence of specific chemical or biological analytes, including common foodborne pathogens such as Salmonella and E.coli. By adding emissive dyes to one of the two immiscible phases of the complex emulsions we were further able to create a ratiometric optical read-out of such a morphology change. We will present how a control over the total internal reflection of light inside droplets creates a platform for using dynamic liquid colloids for the quantification of analytes for sensor applications. This potential of the microcolloids to manipulate light in form of waveguides further leads to the development of new optical transduction methods, where an adjustment of the refractive indices of the solvents results in a new unprecedented control of light propagation inside the emulsion droplets.

COLL 65

Continuous visualization of complex liquid emulsions using on-chip ring resonators

Suchol Savagatrup, *ssavagat@mit.edu*, Timothy M. Swager. MIT, Cambridge, Massachusetts, United States

Complex liquid emulsions are a class of sensors that translate chemical events into observable morphological responses. Recently, we reported selective and sensitive methods to detect the activity of enzymes and the presence of foodborne pathogens. These methods of transduction rely solely on the changes in the optical transmission of the emulsions, which may limit the generality of the analyte. In this presentation, we report the novel approach to continuously sense and quantify the morphology of these emulsions using on-chip ring resonators. The morphological changes of the droplets are visualized by the characteristic of the transmission spectra of the resonators. Specifically, the shift in the resonant wavelength of the ring resonator is highly sensitive to even the small changes in the localized effective refractive indices induced by the morphological switches. By tuning the compositions of the droplets, we demonstrated the on-chip device capability and sensitivity to detect different classes of analytes. We anticipate the combination of complex liquid emulsions and integrated photonics will provide ultra-compact, cost-effective, and generalized method for other chemical and biological sensing schemes.



COLL 66

Modeling of the effect of additives in demulsification of crude oils

Decai Yu¹, dyu@dow.com, **Jonathan Mendenhall**². (1) Dow Chemical, Midland, Michigan, United States (2) Dow Chemical, Lake Jackson, Texas, United States

During the production of crude oil, associated water in the reservoir is often co-produced, forming oil/water emulsions. This water can lead to corrosion and other problems in subsequent pipeline transport and it must therefore be removed. Typically, heat and chemical additives are used to help flocculate and coalesce the water droplets (demulsification). In this work, we modeled the additive assisted demulsification process and examined the behavior of additives at the water-oil interface using molecular dynamics (MD) and dissipative particle dynamics (DPD) simulations. Specifically, we studied the effect of additives on the interfacial tension of water-oil interfaces, and the interaction of additives with surface-active species present in the crude oil. We also examined the displacement of surface-active species by additives and coalescence of additive-coated water droplets using steered DPD simulations. We discuss the advantages of these simulation techniques for investigating interfacial phenomena, but also present some of the shortcomings and areas for potential improvement.

COLL 67

Active demulsification of stable emulsions prepared from mixtures of azobenzene surfactant/SDS using light

Yukishige Kondo¹, ykondo@rs.tus.ac.jp, **Nanami Koizumi**¹, **Yutaka Takahashi**². (1) Dept Ind Chem, Tokyo Univ SCI, Shinjuku, Tokyo, Japan (2) Industrial Chemistry, Tokyo University of Science, Tokyo, Japan

Emulsions are metastable systems where one liquid (dispersoid) is dispersed as particles in another liquid (dispersion medium), and have been used in many fields, including cosmetics and paints. Many research has focused on the enhancement of emulsion stability. On the other hand, Demulsification, which is a phase separation phenomenon of stable emulsions, also plays an important role in industry. For example, aqueous waste fluids containing hazardous substances can be mixed with an oil to obtain an emulsion, and then the emulsion is demulsified to extract hazardous substances into the oil phase. This process is called "emulsion liquid membrane extraction". Demulsification has been so far performed by adding chemicals or by physical techniques such as the application of high electrical fields, or mechanical external forces and the variation of temperature.

In this work, we will focus on the control over the stability of emulsions by an external stimulus, which is light. As a photo-responsive surfactant, a cationic surfactant having an azobenzene group (C4AzoTAB) has been used. When aqueous mixtures of *trans*-C4AzoTAB with SDS and *n*-octane are homogenized, stable oil-in-water (O/W) emulsions are obtained in specific regions of the mole fraction of SDS and surfactant

concentration. UV light irradiation to stable O/W emulsions promotes the *cis* isomerization of *trans*-C4AzoTAB and leads to the demulsification. The difference in surface tension between *trans*- and *cis*-C4AzoTAB aqueous solutions and the measurement of diameters of emulsion droplets indicate that the Ostwald ripening is caused under UV light irradiation and subsequently makes stable emulsions demulsified.

COLL 68

Creating aqueous metastable amorphous dispersions of hydrophobic naphthalene compounds via the “Ouzo effect”

Julie M. Belanger, *juliebelanger@kings.edu*, Joseph Cirilo, Thomas M. Reidy. *Chemistry & Physics, King's College, Wilkes-Barre, Pennsylvania, United States*

Hydrophobic compounds are routinely used in certain biochemical and microbiological assays. These compounds are typically first dissolved in a water-miscible organic solvent, and then added to an aqueous environment. One specific example involves the introduction of naphthalene-based hydrophobic compounds *in vitro* to the membrane bilayer of enveloped viruses for viral inactivation studies. We have discovered that when naphthalene-based hydrophobic compounds are first dissolved in acetone or DMSO, and then subsequently added to water, a cloudy metastable dispersion of particles spontaneously forms. The formation of these dispersions are reproducible and occur at concentrations relevant to the aforementioned assays. The dispersions that form contain spheres (average radius ~400 nm) that are stable for days before a slow-nucleating crystallization occurs. The formation of these dispersions is presumably due to the “Ouzo effect”, named after a Greek drink of the same name. The particles that are suspended in these dispersions result from the initial formation of solution droplets (containing solvent and hydrophobic compounds) that fairly rapidly create supersaturated droplets of solution via solvent-shifting. Various naphthalene-based compounds were studied for their effect to create these dispersions, such as N-phenyl-1-naphthylamine (NPN), 1-iodonaphthalene (INAP), 1,4-dimethoxynaphthalene, 1-naphthol, and 1-aminonaphthalene. Of the compounds studied, only NPN and INAP were found to create “Ouzo-like” dispersions. The formation of these dispersions and characterization using optical and fluorescence microscopy, nephelometry, dynamic light-scattering, and partition coefficient determination will be discussed.

COLL 69

Influence of microfibrillated cellulose fractions on the rheology of water suspensions: Colloidal interactions and viscoelastic properties

Goksu Cinar¹, *cinargoksu@gmail.com*, Per A. Larsson¹, Anastasia V. Riazanova¹, Anni Karppinen², Hans Henrik Øvrebø², Lars Berglund¹, Lars Wagberg¹. (1) *Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Sweden* (2) *Borregaard AS, Sarpsborg, Norway*

The development of sustainable materials that can replace commercial petrochemical based materials is an incitement for collaboration between academia and industry. Different bio-based product alternatives such as polylactic acid, chitosan, starch and gluten have been considered but cellulosic alternatives such as microfibrillated cellulose (MFC) show unique physical and mechanical properties due to the crystalline nature, high specific surface area and the propensity to form fibrous networks even at low concentrations. Shear-thinning and thixotropic behavior of MFC suspensions also makes them suitable candidates as reinforcing elements or rheology modifiers for/in different industrial applications. MFC has shown large promise in applications such as adhesives and coatings, reinforcing elements in construction materials and packaging materials and finally as additives in printing paper grades. On the other hand, its properties are still not fully understood due to the heterogeneous structure in terms of size and surface charge distribution. In this study, we aimed addressing the challenges in the characterization of heterogeneous biomaterials by fractionating. A commercially available MFC was fractionated into four size components using a recently developed approach in which two physical screening steps were combined with an additional centrifugation step to obtain two coarser and two finer fractions. Each MFC fraction was characterized based on their morphology and surface charge. That data was linked to their viscoelastic properties to reveal the contribution of each size fraction to the rheological properties of the unfractionated water suspension. It was shown that the rheology of the MFC fractions was strongly influenced by the size of the components, and the finest fraction enhanced the gel behavior of the MFC suspension which was reflected in the highest storage modulus. Flow characteristics of each fraction were also analyzed, and all fractions showed non-linear flow behavior.

COLL 70

Multiphase water-in-oil emulsion droplets produced via microfluidics as artificial cells

Charles D. Crowe, cdc217@psu.edu, Christine D. Keating. Penn State University, University Park, Pennsylvania, United States

Multiphase artificial cells provide the opportunity to model various complex aspects of eukaryotic cells, including macromolecular crowding, compartmentalization, and localized reaction environments. This research has utilized both neutral polymer phase separation and complex coacervation to produce phase-separated cellular mimics. These aqueous solutions may be emulsified within a continuous oil phase in order to produce a large number of individual, non-interacting droplets, each of which acts as a single experimental instance. However, creating these emulsions by simple vortex mixing yields a heterogeneous population of droplets with a wide range of physical aspects, such as total volume, relative phase volume, and concentration of included solutes. Microfluidics provides a solution to this, giving much finer control over droplet formation. Emulsions produced via a constant microfluidic configuration consist of homogeneous droplets with uniform physical characteristics. Additionally, the morphology of the final droplet may be varied by changing the microfluidic parameters.

This has been demonstrated with an aqueous two-phase system consisting of polyethylene glycol (PEG) and dextran, where the relative volume of the two phases within the final droplets may be controlled by adjusting the flow rates of the individual solutions. Furthermore, several different polyelectrolyte solutions were utilized to produce droplets in which phase separation could be induced via temperature shifts. These experiments also include several distinct continuous oil phases and a wide range of microfluidic settings. The control given by microfluidics in the production of these emulsion droplets represents a way to explore various physical phenomena present within biological systems in a thorough, variable way.

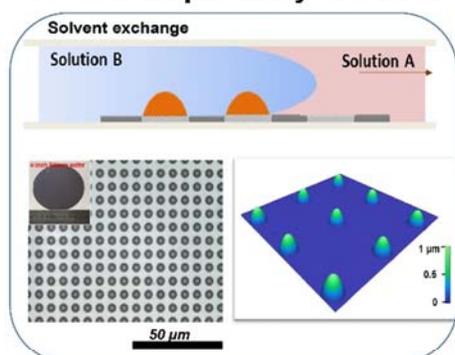
COLL 71

Femtoliter droplet arrays: Formation, dissolution and applications

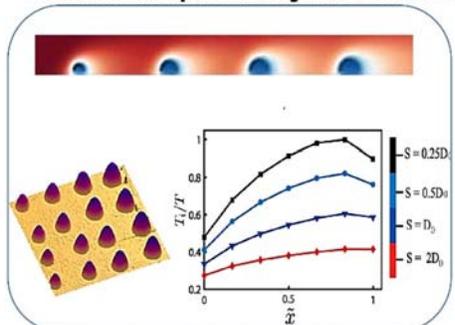
Lei Bao¹, lei.bao@rmit.edu.au, Haitao Yu¹, Vamsi Spandan², Detlef Lohse², Xuehua Zhang³. (1) RMIT University, Melbourne, Victoria, Australia (2) University of Twente, Enschede, Netherlands (3) University of Alberta, Edmonton, Alberta, Canada

Surface droplets immersed in an immiscible liquid phase are essential for a broad range of advanced techniques, such as miniaturized reactors, single biomolecule analysis, near-field imaging, and many others. Controlling the volume and number density of the surface droplets is crucial to achieve high detection sensitivity, high throughput and high resolution in droplet-based applications. In this work, we demonstrate a bottom-up approach to arbitrary control of the size, morphology and positioning of *femtoliter* volume droplets in highly-ordered arrays on an immersed pre-patterned substrate by solvent exchange. Nucleation and growth of the droplets are confined in the planar micropatterns on the surface, which clearly shows a transition of the droplet growth mode from constant contact angle mode to constant contact area mode. The volume and contact angle of the droplet arrays can be tailored through flow conditions and solution concentration. Furthermore, we quantitatively investigate how the lifetime of such femtoliter droplet arrays is influenced by the droplet location relative to the flow direction, drop-to-drop spacing, and the imposed flow rate. Our work clearly reveals coupled effects from droplet collective interaction and the external flow conditions on droplet dissolution in a laminar flow, allowing to form a volume gradient across droplet arrays. The experimental results are in the good agreement with the analysis through our theoretical models that describe droplet array growth and dissolution. As demonstration, we show that controlled formation and dissolution of surface arrays can be applied for droplet-based surface engineering, light manipulation and pollutant exaction in liquid.

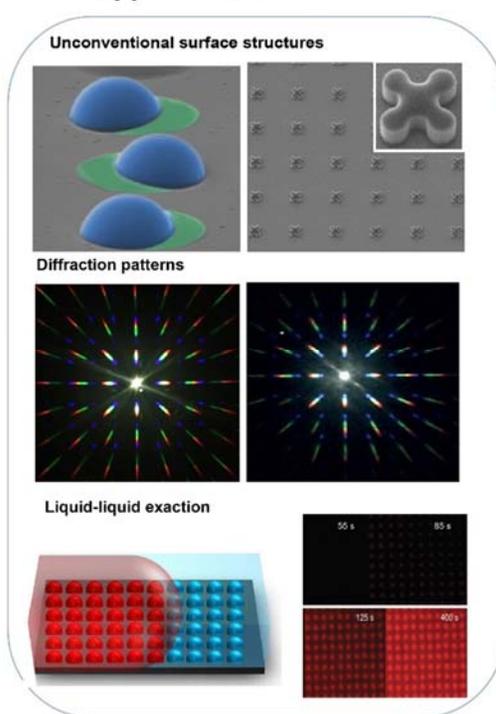
Surface droplet array formation



Surface droplet array dissolution



Applications



COLL 72

Rheology and phase morphology of liquid crystal dispersed silica-core nanoparticles

Marisa Tukpah, Sainath Jadhav, **Ruel McKenzie**, ruel.mckenzie@gmail.com. Polymer Engineering, The University of Akron, Akron, Ohio, United States

The high surface area to volume ratio and interfacial tailorability of nanoparticles typically promotes host matrix property-enhancing functionalities and enables an ever-increasing array of emergent applications in composite systems. To extend these benefits to take advantage of the anisotropic activity of liquid crystals (LCs), challenges such as nanoparticle-induced molecular alignment distortion and LC-induced elastic force perturbation effects must be effectively managed. These issues generally impose limited nanoparticle compatibility with LCs as dispersibility and phase stability are poor, which results in inhomogeneous distribution and particle aggregation, at times in the formation of discrete nanoparticle networks. Strategies to improve dispersibility and solution stability in LCs rely on surface functionalization with mesogen compatible moieties. A range of surface functionalizing agents are surveyed for improving silica nanoparticle compatibility in 4-cyano-4'-pentylbiphenyl (5CB). The effects of surface functionalizing agent and particle size, and their respective concentrations, on the phase morphology and thermal stability of the nanocomposite are examined by means of rheometry and microscopy for phase diagram development. The dynamics of aggregation are highlighted to map the time-scale evolution of phase instability in the nanocomposite with respect to the mesogenic phase. In particular, the surface

functionalizing agents are assessed towards synthesizing hemispheric silica-core Janus nanoparticles to produce anisotropic surfaces capable of directing discrete, phase stable, thermally-triggerable assemblies. Preliminary results on this effort will be presented as a comparative supplement to the discussion on isotropic functionalized nanoparticles and the resultant colloidal meso-phases that manifest from competing effects of LC alignment and elastic forces.

COLL 73

Dynamic structural color in reconfigurable complex droplets

Amy Goodling¹, aeg28@psu.edu, Sara Nagelberg³, Mathias Kolle³, Lauren D. Zarzar^{1,2}. (1) *Materials Science and Engineering*, The Pennsylvania State University, State College, Pennsylvania, United States (2) *Department of Chemistry*, The Pennsylvania State University, State College, Pennsylvania, United States (3) *Department of Mechanical Engineering*, MIT, Cambridge, Massachusetts, United States

Structural color is often seen in nature because of its intense vibrancy and non-diminishing color. The ability to alter the color and optical characteristics through variations in geometric structure or material properties can lead to highly tunable or responsive coloration with applications such as displays and sensors. We describe the iridescent properties of complex emulsion droplets where the coloration is tunable via alterations in the droplet morphology, interfacial curvature, size, and orientation. We explore possible explanations for the optical mechanism and the dynamic characteristics of these fluid, structurally colored droplets.

COLL 74

Templated growth of a chiral thin film oxide

Alex Schilling¹, alex.schilling@tufts.edu, E Charles H. Sykes². (1) *Chemistry*, Tufts University, Medford, Massachusetts, United States (2) *Tufts University*, Medford, Massachusetts, United States

Chiral surfaces are of growing interest in terms of their enantioselective adsorption and reaction properties. While metal surfaces can be prepared with a wide range of chiral surface facets, chiral oxide surface preparation is more challenging. We have studied the “29” copper oxide by oxidizing a Cu(111) crystal at at 650 K. The resulting film takes the form of the “29” oxide which contains six hexagonal rings, five of which contain an oxygen adatom. This specific oxide is called the “29” because it has a unit cell 29 times larger than the Cu(111) unit cell. In order for this oxide film to lie epitaxially on the surface, the rings are compressed in a way that renders the film chiral. Due to the three-fold symmetry of the underlying Cu(111) surface each chirality of the oxide exhibits three rotational domains. Using a surface structure spread single crystal (S⁴C), which has a range of known surface facets as a function of position on the crystal we are able to investigate the mechanism of chiral oxide domain growth. We discovered that

oxidation re-facets the Cu(111) step edges in chiral directions. Furthermore, continuous homochiral domains of the 29 oxide grew in areas where the step edges were <20 nm apart. These results indicate that by careful choice of the Cu metal facet one can grow a single chirality of the “29” copper oxide by virtue of templating by the original metal step edges. This offers the possibility of a new well-defined chiral oxide surface for the study of chiral surface chemistry with scanning probe and temperature programmed desorption studies.

COLL 75

Helical nanoparticle-induced enhancement of molecular optical activity

Lin Yang, niceyanglin@gmail.com. Physics, Hong Kong Baptist University, Hong Kong, Hong Kong

More than 80% of drugs in the worldwide market are chiral drugs, and typically one enantiomer has positive therapeutic effect while another may have side or even fatal effect, due to biomolecular homochirality. It is of fundamental significance to differentiate an enantiomer from its mirror image (i.e., enantiodifferentiation), through monitoring optical activity of, e.g., circular dichroism (CD) denoting differential absorption of left- and right-handed circularly polarized light (CPL) in the UV-visible region. However, sub-wavelength molecular dimensions substantially prevent enantiomers from effectively perceiving the different circular polarization states, leading to low optical activity (OA). In this presentation, a new method will be introduced to enhance enantiomeric OA. Enantiomers are grafted on helical nanoparticles (HNPs) with sub-5-nm helical pitch, which are deposited by glancing angle deposition (GLAD) with fast substrate rotation, leading to an amplification of OA in roughly one order of magnitude. Adsorption configuration of enantiomers are simulated to reveal that the OA enhancement may be ascribed to the supramolecular chiral assembly of the enantiomers on the helical surface, which is sensitive to the helicity of HNPs. This work devices a new method to operate sensitive enantiodifferentiation, which is of urgent demand for chiral pharmaceutical production, food quality control, and environmental pollution monitoring.

COLL 76

Chiral adsorbate assembly in 2D: Racemates or conglomerates

Andrew J. Gellman, gellman@cmu.edu, Soham Dutta. Department of Chemical Engineering, Carnegie Mellon Univ, Pittsburgh, Pennsylvania, United States

Surface chirality is needed to develop functional chiral surfaces for enantiospecific applications. While molecular chirality in 3D has been the subject of study for almost two centuries, many aspects of 2D chiral surface chemistry have yet to be addressed. In 3D, racemic mixtures of chiral molecules tend to aggregate into racemate (molecularly heterochiral) crystals much more frequently than conglomerate (molecularly homochiral)

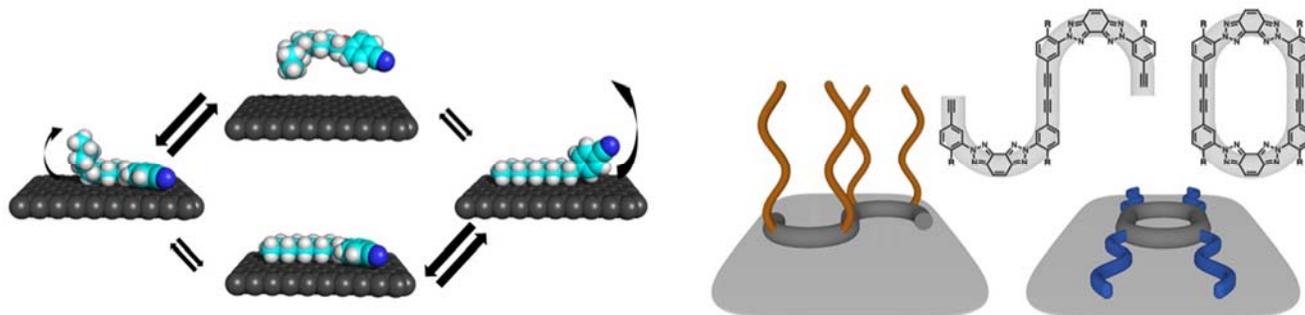
crystals. Whether chiral adsorbates on surfaces preferentially aggregate into heterochiral rather than homochiral domains (2D crystals or clusters) is not known. We have made the first attempt to answer the following question based on available data: In 2D racemic mixtures adsorbed on surfaces, is there a clear preference for homochiral or heterochiral aggregation? The current hypothesis is that homochiral packing is preferred on surfaces; in contrast to 3D where heterochiral packing is more common. We present a simple hierarchical scheme to categorize the chirality of adsorbate-surface systems. We then summarize the findings of a review of the body of work using scanning tunneling microscopy (predominantly) to study aggregation of racemic adsorbates. Our analysis of the existing literature suggests that there is no clear evidence of any preference for either homochiral or heterochiral aggregation at the molecular level by chiral and prochiral adsorbates on surfaces.

COLL 77

Towards understanding and controlling molecular self-assembly

Henry D. Castillo¹, henrcast@indiana.edu, John M. Espinosa Duran¹, Soobin Kim², Dongwhan Lee², Peter Ortoleva¹, Steven L. Tait¹. (1) Department of Chemistry, Indiana University, Bloomington, Indiana, United States (2) Department of Chemistry, Seoul National University, Seoul, Korea (the Republic of)

Programming the self-assembly of organic molecules into highly-organized 2D architectures is a strategy of interest to templating crystalline organic semiconductor thin films. However, this depends on the ability to control precise structural ordering and understand nanoscale molecular processes that occur during self-assembly. To this end, we have selected two prototypical molecular systems to examine at the solution-graphite interface with scanning tunneling microscopy (STM) and with atomistic molecular dynamic (MD) simulations. The first is an alkoxybenzotrile that contrasts van der Waals and local electrostatic interactions, as well as interesting shape and steric interactions, in the self-assembly process. STM was used to determine packing structure and to benchmark force fields and MD. MD simulations revealed the atomistic and sub-nanosecond stages of desorption, reabsorption, and on-surface motion; this provided new insight into molecular level assembly dynamics. Second, the self-assembly of a series of bis(triazolo)benzene-based π -conjugated macrocycles and their flexible precursors were compared. Peripheral functionalization with alkyl and glycol chains resulted in comparable solubility, but self-assembly can be tuned between a tight packing of aromatic cores with desorbed glycol chains or a looser packing of aromatic cores separated by interdigitated alkyl chains. While the macrocycles self-assemble immediately and spontaneously, their flexible linear precursors exhibit slower self-assembly kinetics, due to the large conformational space available to the precursors. STM tip bias or aromatic co-solutes reduced that conformational space and, remarkably, significantly accelerated self-assembly. The observations and from these studies provide insights into the dynamics and design rules of small molecule self-assembly.

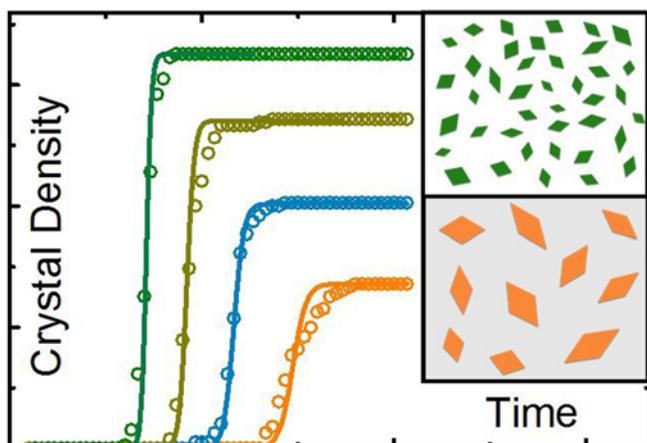


COLL 78

Quantitatively predicting nanoscale domain morphology in solution-processed organic thin films

David L. Patrick¹, david.patrick@wwu.edu, Griffin Reed¹, Linnea Bavik¹, Cyrus SchAAF¹, Brad Johnson². (1) Chemistry, Western Washington University, Bellingham, Washington, United States (2) Physics, Western Washington University, Bellingham, Washington, United States

The electronic and optoelectronic properties of molecular semiconductor thin films are directly linked to nanoscale structural characteristics such as domain size and spatial distributions. In films prepared by solution-phase deposition techniques such as spin casting and solvent-based printing, morphology is governed a complex interrelated set of thermodynamic and kinetic factors that classical models fail to adequately capture, leaving them unable to provide much insight, let alone predictive design guidance for tailoring films with specific nanostructural characteristics. We describe a comprehensive treatment of solution-based film formation enabling quantitative prediction of domain formation rates, coverage, and spacing statistics based on a small number of experimentally-measurable parameters. The model combines a mean-field rate equation treatment of monomer aggregation kinetics with classical nucleation theory and a supersaturation-dependent critical nucleus size to solve for the quasi-two-dimensional temporally- and spatially-varying monomer concentration, nucleation rate, and other properties. Excellent agreement is observed with measured nucleation densities and inter-domain radial distribution functions in polycrystalline tetracene films.



COLL 79

Investigating adsorbed films of linear alkanes on solid surfaces: A thermodynamic, modeling, and scattering study

Nicholas A. Strange¹, *nstrang1@utk.edu*, **Thomas Arnold**², **John Z. Larese**³. (1) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (2) Diamond Light Source, Harwell, United Kingdom (3) Chemistry Dept., University of Tennessee, Knoxville, Tennessee, United States

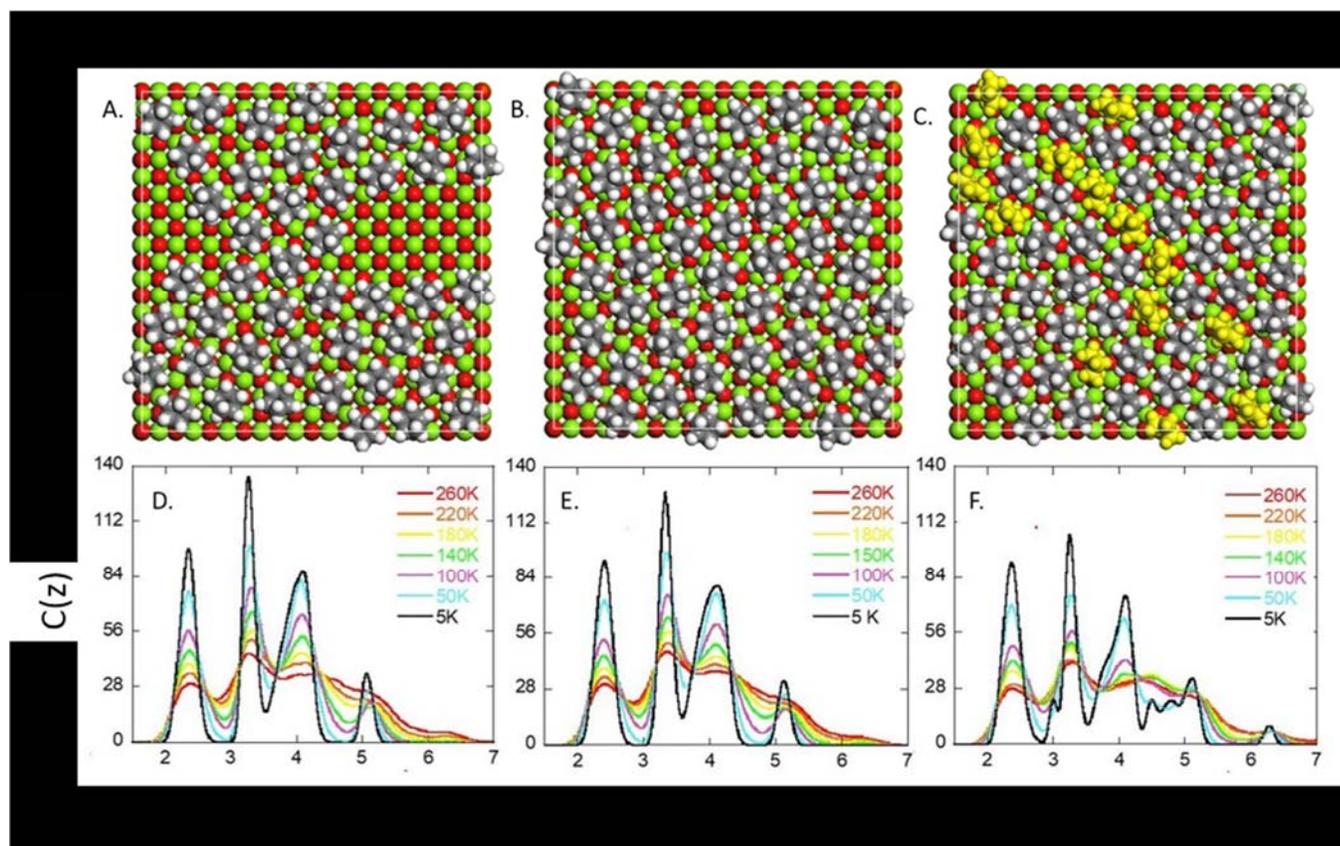
Alkanes play a central role in a variety of technologically important processes including lubrication, separations and purification, catalysis, and liquid crystals. Moreover, there are a variety of surface-catalyzed chemical reactions that involve the adsorption of light alkanes on a substrate. A comprehensive understanding of underlying phenomena that dictate the behavior of alkanes in the adsorbed phase can be obtained by employing a multi-faceted approach including volumetric adsorption, molecular dynamics simulations, and neutron/x-ray scattering techniques. Recently, a study has been completed which characterized the adsorption properties of n-alkanes (methane – decane) on a variety of substrates. High-resolution volumetric adsorption isotherm measurements were performed over a broad range of temperatures near the bulk triple point for n-alkanes adsorbed on MgO(100), graphite, and boron nitride in order to determine the thermodynamics of adsorption. Results from MD simulations provide a microscopic understanding of the monolayer solid structures and resulting dynamics in the adsorbed phase. Distribution functions and transport properties were calculated from the MD simulations in order to make a comparison to experimental results. The microscopic structural properties were determined for several monolayer solid films using neutron / x-ray diffraction.

COLL 80

Adsorption of cycloalkanes on MgO (100), graphite and hexagonal boron nitride: A thermodynamic, modeling and neutron scattering study

Fatema Wahida¹, fwahida@vols.utk.edu, John Z. Larese². (1) Chemistry, University of Tennessee, Knoxville, Tennessee, United States (2) Chemistry Dept., University of Tennessee, Knoxville, Tennessee, United States

The rotational and vibrational behavior of cycloalkanes, e.g. pseudorotation in cyclopentane and the interconversion of the two chair conformations of cyclohexane, have been topics of fundamental interest for several decades. Investigation of the effect of surface symmetry on the physical adsorption properties of thin films of these cyclic molecules is the focus of this study. Understanding how the molecular structure/configuration and dynamics within these films and the effect on the wetting properties has been studied using thermodynamic and molecular modeling methods. High-resolution volumetric adsorption isotherms of cyclopentane and cyclohexane on MgO (100), graphite and hBN basal planes have been recorded over a broad range of temperature (195K-263K). These isotherms were used to determine the adsorption thermodynamic properties (i.e. heats of adsorption, isosteric heats, differential enthalpy and entropy) and to identify regions where phase transitions might occur. Molecular dynamics simulations of mono- and multilayers of cycloalkanes (C3- to C6-) on these surfaces have been used to obtain binding energies, molecular trajectories, pair-correlation functions and Z-distribution of molecules perpendicular to the adsorbing surface plane. These experimental results serve as the prelude to elastic and inelastic neutron scattering experiments. Preliminary investigation of the microscopic film dynamics using neutron spin echo experiments has been performed on sub-monolayer of cyclohexane adsorbed on MgO and graphite. Future neutron diffraction and inelastic neutron scattering studies will be used to investigate the microscopic structure and molecular vibrations in the adsorbed layers. Comparison of the scattering results with the thermodynamic and modeling studies will be presented.



Concentration profile ($C(z)$) of cyclopentane molecules on MgO (100) as a function of temperature and coverage

COLL 81

Application of crystalline substrates for nucleation control and polymorphic selection of Indomethacin

Tharanga K. Wijethunga, tharanga@mit.edu, Xingyu Chen, Allan S. Myerson, Bernhardt Trout. *Chemical Engineering, Massachusetts Institute of Technology, Quincy, Massachusetts, United States*

Due to the inevitable presence of heterosurfaces and favorable energetics, almost all crystallizations are initiated by heterogeneous nucleation. Even though the fundamental mechanistic details are lacking, heterogeneous nucleation is a highly sorted method in industrial crystallizations to control the nucleation kinetics, crystal growth, crystal size distribution, morphology and polymorphism of the desired compound. In particular, controlling polymorphism and discovery of novel polymorphic forms by applying heterosurfaces is of significant interest due to the physicochemical property variations that polymorphs can exhibit. In this study, we studied the nucleation kinetics and applied selected crystalline herosurfaces for the polymorphic control of indomethacin. To this end, we selected six organic functional crystalline substrates, L-Glutamic acid (GLU), L-

Threonine (THR), Allantoin (ALT), Xanthine (XAN), Biotin (BIO) and L-Histidine (HIS) and Sodium Chloride (NaCl) as substrates. The effectiveness of each substrate in enhancing the nucleation rates of indomethacin was examined with a high throughput microscopic method and polymorphic selection towards each form of IMC was investigated with a combination of microscopy and Raman spectroscopy. Furthermore, we conducted Raman spectroscopy based crystal face indexing to identify the in contact faces for the substrate and IMC. This work aims to elucidate the role of intermolecular interactions and substrate functional groups at the substrate-solution interface in driving the nucleation kinetics and polymorphic selection in general. We expect this extension of fundamental understanding to provide the opportunity to rationally affect the nucleation stage with the aid of intentionally added well-defined crystalline heterosurfaces and to improve the control over the desired crystal properties.

COLL 82

High-throughput study of the role of spatial organization on the activity of surface-bound enzymes

Nourin Alsharif¹, nourin@bu.edu, Timothy Lawton², Joshua R. Uzarski², Keith A. Brown^{1,3}. (1) Mechanical Engineering, Boston University, Boston, Massachusetts, United States (2) Natick Solider Research Development and Engineering Center, Marlborough, Massachusetts, United States (3) Physics, Boston University, Boston, Massachusetts, United States

Nature precisely localizes enzymes across several length scales. *In vivo*, many intracellular reactions are catalyzed by membrane-bound complexes that not only consist of multiple precisely oriented enzymes but are also specifically arranged within the cell as a whole. In order to best utilize enzymes in an *ex vivo* setting, the role of this multiscale organization must be understood. Here, we report a novel strategy for studying the activity of arrangements of enzymes in a high throughput manner. In particular, we use top-down patterning techniques in conjunction with small molecule self-assembly to designate enzyme-binding regions amidst a non-binding background. Key to this experimental scheme is the parallel nature of both the fabrication and the characterization processes that enable the efficient study of many geometric parameters of the enzyme-binding features. These parameters include, (1) feature size, (2) density of enzyme within each feature, and (3) distance between features. This level of control can in principle allow us to separate effects of reaction kinetics and substrate diffusion. Two strategies have been explored for the immobilization of enzymes including click chemistry to non-natural amino acids and binding to poly-histidine affinity tags. Top-down lithography and enzyme assembly were verified using a variety of surface characterization techniques including atomic force microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy, spectroscopic ellipsometry, and contact angle goniometry. Initially, this high throughput paradigm is used to develop a fluorometric assay to quantify the activity of surface-bound enzymes as a function of their spatial organization. Together with the widespread utilization of high throughput

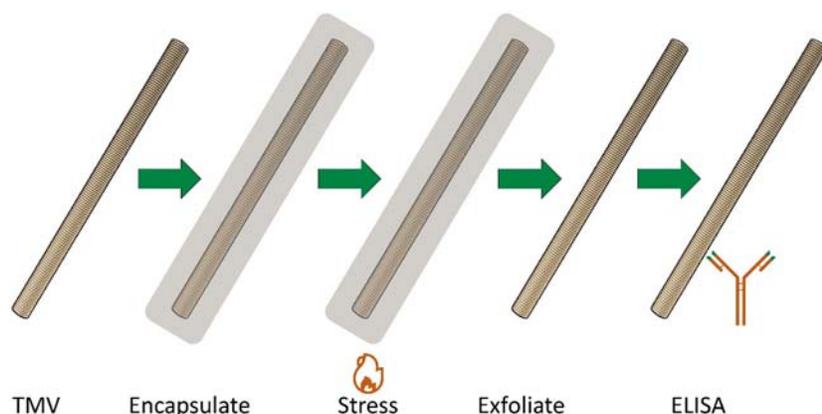
techniques in synthetic biology, the ability to study spatial organization in a rapid fashion is expected to dramatically improve *ex vivo* applications of enzymes.

COLL 83

Immunoassay investigation of vaccine carrier stability within ZIF-8 encapsulation

Raymond P. Welch, *rpw031000@utdallas.edu*, Michael A. Luzuriaga, Shaobo Li, Jeremiah J. Gassensmith. *Chemistry and Biochemistry, University of Texas at Dallas, Dallas, Texas, United States*

Proteinaceous drugs often require constant refrigeration, from point of manufacture through transportation, storage, and ultimately administration in a patient. Failure of the refrigeration system at any point can lead to loss of drug activity or function and subsequent increased costs in money, time, material, and health. This hits harder in regions of the world that lack sufficient infrastructure to maintain refrigeration due to location in a developing nation, remote or inhospitable geography, disaster area, or warzone. Recent studies have shown that enzymes, antibodies, and even entire virus particles can be encapsulated in a ZIF-8 coordination polymer that provides thermal, mechanical, and chemical stability to the underlying proteinaceous material. A recent study has shown the viability of encapsulating individual tobacco mosaic virus (TMV) particles within a ZIF-8 shell of tunable thickness, providing morphological and chemical stability against various organic solvents and boiling water, with stability increasing with shell thickness. Because of the high porosity inherent to ZIF-8 reactants in bioconjugation reactions are still able to diffuse through the shell and react with the virus surface, attaching important functional handles for further modification and application. The ZIF-8 shell can also be exfoliated and intact naked virus particles recovered. The aim of the current study is to ascertain the surface stability of TMV through the encapsulation and exfoliation process, including various stressors such as heat and denaturing solvents applied while encapsulated. This is done via enzyme-linked immunosorbent assay, taking advantage of the property of antibodies to bind to specific shapes; a damaged surface will bind less antibodies than an intact one, and when compared to fully intact and fully denatured surfaces, the stress on the surface can be measured. Also tested is the ability to infect plants through the process, and antibody production in mice against the encapsulated virus.



TMV through the process of encapsulation in ZIF-8, stress, exfoliation, and immuno assay

COLL 84

Physical chemistry of nanocrystals with the graphene liquid cell

Paul Alivisatos, paul.alivisatos@berkeley.edu. University of California, Berkeley, Berkeley, California, United States

Colloidal nanocrystals have emerged as a major building block for nanoscience and nanotechnology. Today it is possible to control the size, shape, and topology of nanocrystals and to harness the variations of their properties with size to create materials with proven applications in biological imaging and electronic displays, and many more applications under development in renewable energy. Despite these advances, there is much we still do not know about nanocrystals. The advent of *in situ* liquid cell electron microscopy and especially the graphene liquid cell, have opened the door to a series of new experiments that reveal key aspects of the physical chemistry of nanocrystals. This includes the first structural determination of the positions of all the atoms in a colloidal nanocrystal; methods for directly imaging and tracking individual nanocrystals as they grow or dissolve; and the ability to measure the inter-particle potentials by observing pairwise relative motions. These new tools are enabling a second revolution in the science of nanocrystals, as they will permit to us to quantitatively control artificial colloidal nanoscale building blocks with atomic precision.

COLL 85

Understanding the growth and dissolution of metal nanoparticles using *in situ* liquid transmission electron microscopy

Hong Yang, hy66@illinois.edu. Chem. Biomol. Engr., Box C-3, MC-712, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Recent development of liquid cell technology for transmission electron microscopy has created opportunities to study the nanostructures in reaction media at true nanometer (nm) and sub-nm length scale. This new capability allows for quantitative analysis of nucleation and growth, and nanoparticle assembly in real time, thus the growth kinetics. In this presentation, I will use the noble metal nanoparticles as examples to discuss our recent understanding of the kinetics of several processes. The major focus will be on the heterogeneous growth of core-shell nanoparticles based on the Lifshitz-Slyosov-Wagner (LSW) theory, the dissolution kinetics of faceted nanoparticles based on the power law analysis, and methodology development for analyzing ensembles of gold nanoparticles under fluid flow conditions involving the use of a staged coalescence model.

COLL 86

Characterizing formation, growth, dissolution, and transformation of nanocrystals in suspensions

*Jennifer A. Soltis², Nathan D. Burrows³, Virany Yuwono¹, Sandeep Kumar⁵, Amanda M. Vindedahl⁴, Kairat Sabyrov⁶, **R Lee Penn¹**, rleepenn@umn.edu. (1) Chemistry, University of Minnesota, Minneapolis, Minnesota, United States (2) Pacific Northwest National Lab, Richland, Washington, United States (3) Department of Chemistry, Pennsylvania State University, State College, Pennsylvania, United States (4) University of Minnesota, North Saint Paul, Minnesota, United States (5) Intel Corporation, Hillsboro, Oregon, United States (6) Lawrence Berkeley National Lab, Berkeley, California, United States*

Electron microscopy is a powerful technique for elucidating the mechanisms of crystal formation, growth, dissolution, and transformation. We employ cryogenic transmission electron microscopy (TEM) and in situ TEM; in combination with conventional TEM, dynamic light scattering, X-ray diffraction and scattering, UV-visible spectroscopy, as well as kinetic modeling; to elucidate the fundamental processes that govern the kinetics of crystal growth and phase transformations. Each of these techniques has advantages and limitations, and a combination of methods is essential.

COLL 87

Investigating crystal nucleation, transformation and assembly via liquid and cryogenic TEM

***James J. De Yoreo^{1,2}**, james.deyoreo@pnnl.gov. (1) Physical Sciences, Pacific Northwest National Laboratory, Richland, Washington, United States (2) Materials Science, University of Washington, Seattle, Washington, United States*

The classical picture of nucleation envisions addition of monomeric species to a growing nucleus that exhibits the bulk crystal structure. However, recent observations reveal diverse hierarchical pathways involving higher-order species ranging from multi-ion

complexes to dense liquid droplets. These often form an initial disordered phase that transforms to the final ordered phase. Introduction of additives that are either incorporated or act as surface adsorbates can redirect pathways and select for non-equilibrium phases and morphologies. Our knowledge of these multi-stage pathways, the factors leading to their selection and the role of additives has been limited by a lack of *in situ* observations. Here we use liquid and cryogenic TEM to decipher pathways and controls on nucleation, transformation and assembly for calcium carbonate and iron oxide, both of which exhibit multiple polymorphs and often form transient disordered phases. All common crystalline polymorphs of CaCO_3 are observed to form directly and grow to macroscopic size, but when amorphous calcium carbonate (ACC) forms, its fate lies in dissolution due to nucleation of crystalline forms either independently or heterogeneously on the ACC. Introduction of additives produces three distinct outcomes. Some, like citrate and poly-acrylate, extend ACC lifetimes or timescales for dissolution. Highly charged anionic polymers like polystyrene sulfonate sequester Ca to produce globules within which ACC then forms exclusively. High Mg concentrations create a unique pathway by which water-rich ACC transforms isomorphically to Mg-calcite concomitant with expulsion of water. Oxalate addition to FeOx solution leads to formation of spindle-shaped hematite (hm) from an initial ferrihydrite (fh) phase. The spindles are elongated along $\langle 001 \rangle$ and consist of atomically aligned domains organized into second-order, hierarchical, rod-like structures penetrated by nm-scale pores. This structure does not result from fh assembly or even growth by oriented attachment of hm that nucleates randomly in bulk solution and then diffuses to the spindle. Rather, a small number of hm seeds form from fh and then trigger an interface-driven autocatalytic process by which new hm particles repeatedly form immediately adjacent to existing ones and attach to the growing spindle. The result highlights how the broken symmetry of the interface can alter ion distributions, chemical potentials and inter-particle forces driving crystallization.

COLL 88

Visualizing nanoscale assembly and elastocapillary effects in solution using *in situ* TEM

Utkur Mirsaidov, *mirsaidov@gmail.com*. *Physics, National University of Singapore, Singapore, Singapore*

Self-assembly of nanoparticles (NPs) is an important bottom-up nanofabrication method in which NPs spontaneously organize into ordered superstructures. The collective behavior of NPs in assemblies leads to optical, electronic, and mechanical properties that are distinct from those of the bulk materials and individual NPs. NP self-assembly within solutions is driven by intermolecular forces between NPs and external forces. However, owing to experimental challenges associated with imaging nanoscale dynamic processes in liquids, the interaction and assembly mechanisms of NPs are poorly understood.

Here, using direct *in situ* TEM imaging in liquid phase, I will describe the role of intermolecular forces, such as van der Waals, electrostatic forces, solvation, capillary,

and other interactions in NP self-assembly in solution. For example, I will show how the balance between the repulsive hydration force and attractive van der Waals (vdW) force for interacting NPs regulates their attachment dynamics. I will also highlight how chemical functionalization of NPs can guide their self-assembly and the different pathways through which these NPs assemble.

Moreover, I will share our recent results on nanoscale elastocapillary effects that lead to collapse and aggregation of vertical nanowire arrays. I will describe the pathways through which drying, deflection, and adhesion of nanowires occurs and show that the formation of liquid nanodroplets is a common intermediary in the nanoscale pattern collapse.

Our findings the role of solvent-mediated physical and chemical forces in the assembly of nanoscale materials highlight the importance of direct nanoscale observation in uncovering previously unknown intermediate states that are pivotal for synthesis and self-assembly.

COLL 89

Atomistic modeling of nanoparticle self-assembly in liquid cells and at liquid interfaces

Petr Kral, pkral@uic.edu. University Illinois Chicago, Chicago, Illinois, United States

First, we discuss the modeling of dynamical in situ experiments revealing the growth and self-assembly of nanoparticles in liquid cells. Dynamical observations reveal important details about the self-assembly mechanisms which allow us to develop more precise models and overall understanding of these systems. In this manner we can disclose almost in each experimental setup a different balance of forces guiding the self-assembly, often contradicting simple expectations from mean-field models. Second, we model the self-assembly of nanoparticles at liquid interfaces, also done in the presence of external magnetic fields. Here, our precise modeling reveals a highly significant role of the liquid in guiding the self-assembly of nanoparticle superlattices. The NP-liquid binding energies are very large, so they fully control the formation of bottom layers in the formed superstructures. We show why very similar solvents can provide very different self-assembly conditions. Finally, we also present the magnetic properties of the self-assembled nanoparticles (hysteresis curves), showing the importance of disorder for these properties. Recently observed superstructures, self-assembled in bulk and at liquid interfaces, will be discussed.

COLL 90

Cryo-electron microscopy: 2D and 3D visualization of nanobubbles, nanoparticles, and supramolecular assemblies

Phoebe L. Stewart, pls47@case.edu. Pharmacology, Case Western Reserve University, Cleveland, Ohio, United States

Cryo-electron microscopy (cryoEM) offers a powerful way to visualize a variety of nanoscale particles and supramolecular assemblies. The cryoEM approach involves flash freezing a sample in a cryogen to preserve nanoparticles in an amorphous frozen layer of water or solvent. Imaging in a transmission electron microscope is performed with a low dose of electrons to avoid destruction of the frozen sample. CryoEM images of gas-filled nanobubbles can provide information on morphological features before and after destruction with high intensity ultrasound. Fourier transforms of cryoEM images can reveal the presence or absence of crystalline order in supramolecular assemblies. CryoEM images will be presented of nanoscale lipid and polymer-stabilized perfluorocarbon gas bubbles with potential for drug delivery, and supramolecular assemblies formed by plant viruses with charged polymeric dendrimers being designed for applications in photon management.

When a cryoEM specimen has a homogeneous structure, 3D single particle reconstruction can be performed. This involves averaging 2D projection images of different particles to generate a 3D structure. A cryoEM reconstruction will be presented of a virus-like particle-polymer conjugate. The 3D structure shows the general conformation of water-soluble polynorbornene polymeric chains attached to a viral capsid. The extent of the interaction between the polymer and the capsid is revealed, providing insight into the shielding properties of the polymer from capsid-specific antibodies. When a cryoEM specimen is heterogeneous, cryo-electron tomography (cryoET) provides an alternate way to generate a 3D structure. This involves collection of a tilt-series of 2D projection images for a defined sample area and generation of a 3D tomogram. Examples will be presented illustrating the application of cryoET to binary mixed polymer brush-grafted silica nanoparticles in aqueous and organic solvents; elongated plant virus-based nanoparticles for enhanced delivery of thrombolytic therapies; and serum albumin-camouflaged tobacco mosaic virus nanoparticles.

COLL 91

Seeing is believing - from crystallizing of nanoparticles to crumpling of polymer films

***Qian Chen**, qchen20@illinois.edu. Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States*

Our research focuses on understanding the organization of complex materials and biological systems in space and time. In this talk, I will discuss two types of systems imaged using electron microscopy-based methods. The first system concerns the crystallization kinetics of a series of nanoparticle superlattices formed in solution. We are able to monitor, for the first time, the initial nucleation of crystallites on the fly in real-time and real-space with low-dose liquid-phase transmission electron microscopy. Single-particle tracking, statistical mechanics-based analysis and Monte Carlo simulations reveal unexpected crystallization kinetics due to inherent many-body coupling and discreteness of building blocks at the nanoscale. In the second system, we investigate the crumpling of a polymer membrane used for water desalination and

filtration. Their three-dimensional morphology has intricate indications on their performances, particularly solvent permeation and solute retention. Both systems serve to achieve our common goal of deciphering fundamental rules of organization from “seeing is believing”.

COLL 92

Membranes with controlled 2D MXene lateral flake sizes

Yury Gogotsi, *gogotsi@drexel.edu. Drexel Univ, Philadelphia, Pennsylvania, United States*

Two-dimensional (2D) transition metal carbides and nitrides (MXenes) are a family of materials synthesized by top-down selective etching of an atomic layer from layered ternary carbides (MAX phases). The resulting materials have demonstrated flexibility, mechanical stability, hydrophilicity, high electronic conductivities and intercalation of cations and/or large organic molecules, spurring interest in their application for ion sieving, gas separation, filtration and water purification. Additionally, MXenes are solution-processed, so they can be synthesized in scalable quantities up to 100 g batches at high concentrations. Consequentially, the as-produced colloidal solutions contain flakes with a wide lateral size distribution (from hundreds of nanometers to several micrometers). The polydispersity in lateral size results in heterogeneous properties, necessitating processing techniques which can isolate 2D materials based on size or thickness.

Here, solution-based size selection and separation techniques, such as sedimentation-based differential and density gradient centrifugation, will be discussed for fabrication of free-standing MXene membranes with controlled flake sizes. The lateral size-property dependence is observed for example in free-standing membranes fabricated with smaller flakes, which exhibit a higher resistance than membranes with larger flakes. Furthermore, membranes composed of Ti_3C_2 nanosheets have already shown potential in selectively sieving gases, such as H_2 , and various alkali, alkaline earth ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}), metals (Ni^{2+} and Al^{3+}), and dye cations (MB^+) based on charge and size without sacrificing water flux rate. The high aspect ratio of the flakes allows for the fabrication of membranes with uniform and narrow 2D nanochannels, which in conjunction with control over the lateral size provides valuable insight on the mechanism of transport of ions and molecules for various applications.

COLL 93

Gas permeation through Pickering membranes

Matthias M. Krejca, *matthias.krejca@chemie.tu-chemnitz.de, Werner Goedel. Physical Chemistry, Chemnitz University of Technology, Chemnitz, Germany*

As described by Pickering in 1907, particles spontaneously adsorb to the surface of droplets and emulsify them for a long period of time (so-called Pickering emulsions).

This effect can be enhanced by giving the particle a hydrophilic and a hydrophobic region (Janus particles). These particles arrange themselves preferably at interfaces between two non-miscible fluids.

Our idea is: We increase the number of regions on the surface of the particles by one. Liquid films should be able to be stabilized by these particles instead of spherical droplets. We regard these films as membranes and call them Pickering membranes, and we call the particles we use for this approach Saturn particles.

The used Saturn particles are produced by masking the caps of hydrophobically coated silica particles and etching the equatorial region in between them via hydrofluoric acid in one step.

In our experience, it is far easier to create such water films stabilized by Saturn particles in air than in a hydrophobic fluid. We do this by suspending Saturn particles in ultrapure water and pumping air bubbles into the water from below. A Pickering membrane is formed. The Saturn particles self-assemble in the water film and protrude it on both sides (see Fig. 1). The Saturn particles stabilize the water film for several days. When replacing the air above the Pickering membrane with one of two gases (CO_2 or SF_6), the gas or air permeates through the stabilized water film and the Pickering membrane moves. When replacing the gas with air, the Pickering membrane moves back again (see Fig. 2). We capture the movement of the Pickering membrane on video to determine the movement speed and therefrom calculate the experimental permeance in quite good agreement with theoretical predictions.

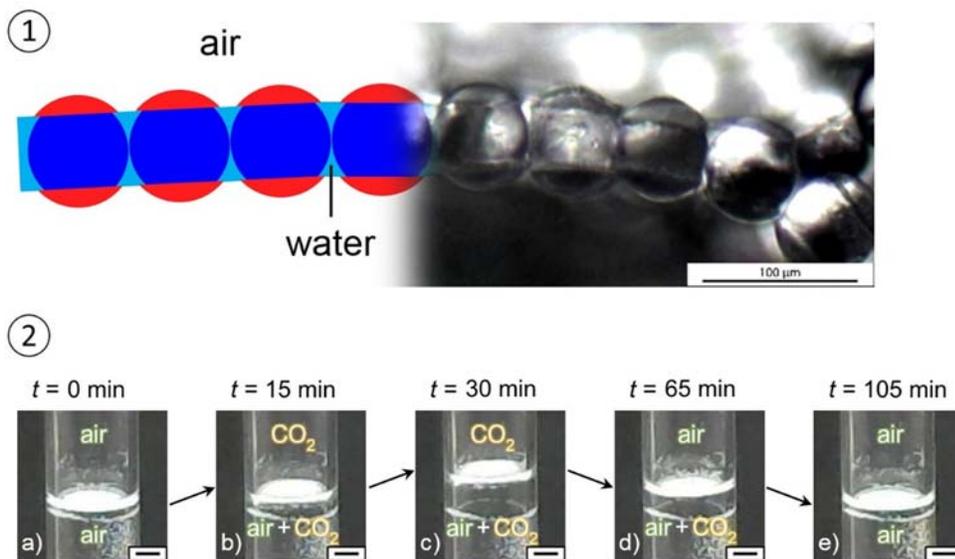


Fig. 1: Sketch and light microscope picture of a Saturn particle stabilized Pickering membrane.

Fig. 2: The permeation of CO_2 through a Pickering membrane. The CO_2 above the membrane permeates through it (a–c). The CO_2 is replaced by air after 30 min. The CO_2 below the membrane permeates back through the membrane until there is only air left (c–e). Scale bar is 2 mm.

COLL 94

Oxidant-triggered rapid deposition of plant-derived phenols on PVDF membrane with ultrahigh water permeability for effective oil/water separation

Yulan Chen, yulan@ualberta.ca, Qingxia Liu. University of Alberta, Edmonton, Alberta, Canada

Membranes with special wettability are ideal candidates for the remediation of oily wastewater; however, fabricating superwetting membranes with facile and low-cost processes still remains a challenge. Herein, a one-step, inexpensive and effective method was developed for fabricating superhydrophilic polyvinylidene fluoride (PVDF) porous membranes via the sodium periodate-induced rapid polymerization and deposition of plant-inspired adhesive catechol (CA). Compared to the traditional processes and other advanced methods reported to date, our protocol shows much faster deposition rate and enhanced surface properties. The as-modified membranes exhibit superhydrophilicity with ultrashort time of wetting and superior underwater oleophobicity, applicable on separation for both oil–water mixtures and surfactant-stabilized oil-in-water emulsions. The optimally prepared membranes, with 2-hour deposition of catechol, show an extremely high water permeability (over $21000 \text{ L m}^{-2} \text{ h}^{-1}$ under 0.075 MPa) and outstanding separation efficiency ($> 99\%$). More importantly, the optimum membranes also show excellent operational stability and antifouling property for long term use, making them a promising technology in purifying wastewater. Due to the chemical versatility of catechol, we envision that this novel coating technique holds significant potentials in tailoring the surface properties of various substrates for a wide range of applications.



COLL 95

Enrichment and recovery of mammalian cells from contaminated cultures using aqueous two-phase systems

Christopher J. Luby¹, *christopher.luby@tufts.edu*, **Benjamin P. Coughlin**¹, **Charles Mace**². (1) *Chemistry, Tufts University, Medford, Massachusetts, United States* (2) *Tufts University, Medford, Massachusetts, United States*

Cell culture is a crucial part of biomedical research in both academia and industry. In vitro cell culture models allow biological systems to be studied and drugs to be developed while reducing the need for animal models. Sterile technique is necessary to ensure that only the cells of interest are growing in the cultures. Contamination, however, is still a relatively common occurrence in cell culture laboratories. Typical contaminants include bacteria, yeast, and mold. These microorganisms can affect the way cells behave in culture and alter the culture conditions by changing the pH or by competing with the cells for resources. Dead cells can also contaminate cultures by distorting cell counts or signaling other cells to die. Contaminants typically have different buoyant densities from the cultured cells. We exploited this difference and developed a method to separate cultured mammalian cells from contaminants on the basis of density using aqueous two-phase systems (ATPS). We tuned the properties of a 7% w/w polyethylene glycol (PEG)–11% w/w Ficoll ATPS to prepare a biocompatible system that removes contaminants and isolates desired cells at the liquid-liquid interface with little to no adverse effects on the viability or growth of the cultured cells. This system can be used to enrich cell culture populations for viable cells and to reduce the number of microorganism contaminants in a culture, which increases the chances of subsequent antibiotic treatments being successful. We tested the effectiveness of our method in model contaminated cultures of both adherent (HeLa) and suspension (HL-60 II) mammalian cells contaminated with bacteria (*E. coli*), yeast (*S. cerevisiae*), and nonviable cells.

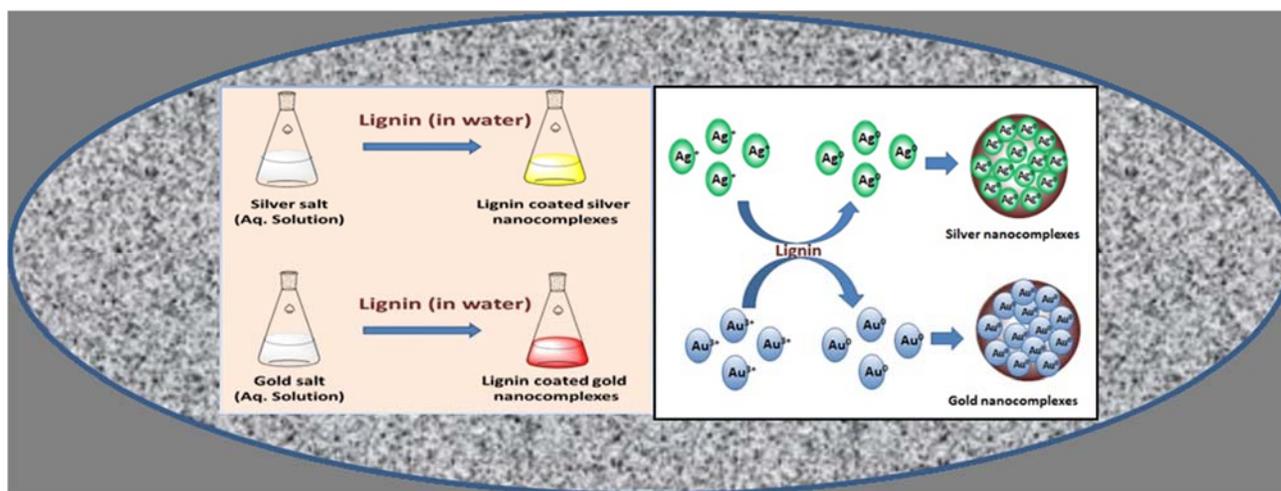
COLL 96

Development of nanolignin complexes from lignocellulosic biomass for applications in nanobiotechnology

Jayeeta Bhaumik, *jbhaumi@gmail.com*, **Sanjam Chandna**, **Ravneet Kaur**, **Y. Nikhileshwar Reddy**. *Center of Innovative and Applied Bioprocessing, Department of Biotechnology (Govt. of India), Mohali, Punjab, India*

A major source of aromatic renewable resources is agricultural biomass. Through the development of biocompatible nanomaterials from lignocellulosic biomass, the huge amount of agricultural waste generated every year can be significantly reduced which in turn will benefit the environment. Lignin is present in vast quantities in the agricultural biomass and is known to be an important source of polyphenols. Lignin, therefore, has the potential to cater as a biodegradable component for nanomaterial formulation. Due

to the biocompatibility along with antioxidant properties, lignin derived nanocomplexes can be employed in various nanobiotechnology applications. Lignin derived metal and metal oxide nanocomplexes (LMNPs) were developed via green methodology. Lignin (obtained from agricultural waste) based nanocomplexes were further characterized by absorption spectroscopy, dynamic light scattering and transmission electron microscopy. Surface of the LMNPs were functionalized with various diagnostic and therapeutic agents as well as enzymes via conjugation chemistry. Lignin derived LMNPs were examined for antioxidant properties for possible biomedical applications. The newly developed nanolignin complexes have enormous potential for multiple nanobiotechnology applications including biomedicine. Furthermore, these lignin-derived nanocomplexes will serve dual purposes by reducing environmental pollution as well as by being applicable in versatile sectors including nanomedicine.



Lignocellulosic Biomass Mediated Metal Nanocomplexes

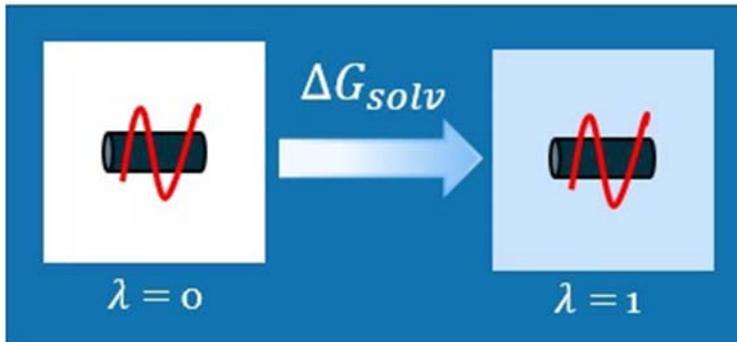
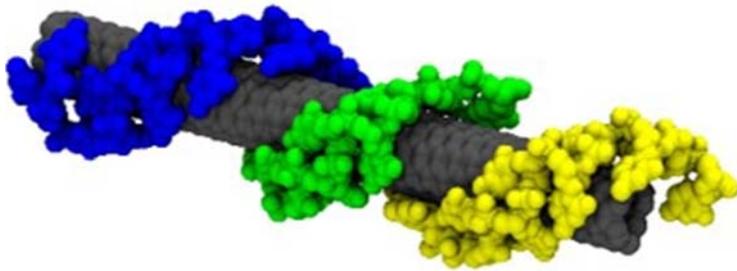
COLL 97

Ranking binding affinity for ssDNA-wrapped single-walled carbon nanotube (SWCNTs) using free energy perturbation (FEP)

Kevin Hinkle, Frederick R. Phelan, frederick.phelan@nist.gov. STOP 8542, NIST, Gaithersburg, Maryland, United States

A novel separation strategy that has recently emerged for separating single-walled carbon nanotubes (SWCNTs) by chirality is the use of aqueous two-phase extraction (ATPE) in conjunction with single-stranded DNA (ssDNA) as a dispersant. It has been found experimentally that certain ssDNA sequences have greater binding affinity to specific SWCNT chiralities enabling efficient isolation of single species from the highly heterogeneous mixtures inherent to the synthesis process. The challenge in this has been the identification of ssDNA-SWCNT, sequence-chirality pairs that are optimal binders. This has led to a lot of immense amount of trial and error work on the experimental end to develop even a small library of matches.

In this talk, we describe a new protocol using molecular simulations and free energy perturbation (FEP) that can be used to quantify and rank the binding affinity of ssDNA-SWCNT pairs based on differences in their free energy of solvation. To test the method, we study the ssDNA-SWCNT binding process for both optimal and non-matching binding pairs and find that the ranking of ssDNA sequence binding affinity relative to specific SWCNT chiralities matches very well with experimental observations. We also study the effect of the relative concentration of ssDNA and use that information to quantify the effect of inter- and intra-strand ssDNA hybridization on the free-energy – this yields insight into the physics driving the stability of the binding process. Future work to use the new protocol to design optimal binding pairs will also be described.



COLL 98

Impact of operating conditions in membrane-based separation processes on the characteristics of inorganic scales on membrane surface

*Omkar Lokare, Shardul Wadekar, **Radisav D. Vidic**, vidic@pitt.edu. University of Pittsburgh, Pittsburgh, Pennsylvania, United States*

Membrane based separation processes have become an integral part of water treatment and reuse industry. Even though the mode of operation and driving force for different membrane based separation processes may be different, all are affected by membrane scaling at high water recoveries that increases mass transfer resistance and greatly affects performance. Previous studies evaluated the fouling behavior in pressure-driven processes and thermally-driven processes (i.e., membrane distillation) separately and the comparison was mostly qualitative. Pressure-driven processes experience a severe flux decline due to scaling while the fouling layer in membrane

distillation may be quite porous and have a much lower impact on system performance. We quantitatively studied the difference in the fouling process in pressure-driven (nanofiltration, NF) and thermal membrane processes (direct contact membrane distillation, DCMD). Preliminary results indicated a severe decline in NF permeate flux when treating real abandoned mine drainage while DCMD exhibited negligible flux decline with the same wastewater. To further investigate this phenomenon, fouling in DCMD and NF was compared using calcium sulfate and calcium carbonate as foulants under identical experimental conditions (i.e., ionic strength, temperature, hydrodynamic conditions, water recovery, and scale mass). CaSO_4 resulted in instantaneous permeate flux decline (i.e., 89%) followed by a further decrease of 52% over 12 hours with NF. CaSO_4 scaling in the case of DCMD occurred after 2 hours and no initial flux drop was observed. However, the flux decreased by 67% over the next 12 hours accompanied by membrane wetting. Imaging of the scales indicated uniform needle-like CaSO_4 crystals on DCMD membranes and patchy flat needles on NF membranes. The differences can be explained by the 40-fold difference in the operating feed pressures in the two processes. On the other hand, CaCO_3 fouling occurred instantaneously in both DCMD and NF processes. However, permeate flux decline in DCMD was only 17% and remained constant over the next 12 hours while continuous flux decline with time was observed in NF. Results of the ongoing tests to explain the impact of membrane fouling on the flux and rejection efficiency with two different membrane processes will be presented at the conference.

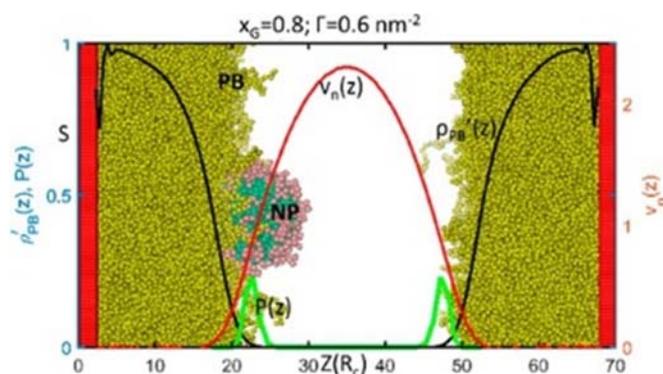
COLL 99

Mesoscale simulations of nanoparticle separation on polymer-grafted porous media

Aleksey Vishnyakov^{1,3}, shibboleth@list.ru, Santo Kolattukudy Poulouse², Alexander V. Neimark⁴, Yefim Brun⁵. (1) Department of Chemical and Biochemical Engineering, Rutgers University, Piscataway, New Jersey, United States (2) Department of Chemical and biochemical Engineering, Rutgers University, Piscataway, New Jersey, United States (3) Center for Computational and Data Intensive Science and Engineering, Skolkovo Institute of Science and Technology, Moscow, Russian Federation (4) Rutgers Univ, Piscataway, New Jersey, United States (5) Central Research & Development, DuPont, Wilmington, Delaware, United States

The presentation describes an effort to develop foundations of interactive nanoparticle chromatography (INPC) using coarse-grained simulations. INPC is a novel experimental technique for nanoparticle (NP) separation by size or by the surface chemistry. The latter, size-independent separation is very important practically but quite challenging: particles with similar surfaces should elute from a chromatographic column at the same time. It is suggested that a size-independent separation can be achieved on columns modified with polymer brushes (PB); the interactions between the brushes and particles depend on their surface chemistry. In this work, coarse-grained simulations are employed to examine the free energy landscapes of functionalized NPs inside PB-grafted channels depending on the solvent composition, PB grafting densities and NP

surface, which is varied via the composition of short ligands attached to the NPs. The free energy landscape determines NP partitioning between the stationary phase of PB and the mobile phase of flowing solvent. We analyze the transport of nanoparticles through a polymer-grafted channel and calculate the mean velocity and retention time depending on the particles size and solvent composition. It is shown that with the increase of poor solvent fraction and respective PB contraction, NP separation exhibits a transition from the hydrodynamic size exclusion regime with larger NPs having shorter retention time to the adsorption regime with smaller NPs having shorter retention time, and the location of this transition depends on the NP surface. This finding suggests the possibility of the existence of a special regime in INPC at which NPs with like surface properties elute together regardless of their size. The latter has important practical implications: NPs can be separated by surface chemistry employing the gradient mode of elution with controlled variation of solvent composition.



Functionalized nanoparticle in a channel with walls covered by a polymer brush. Lines: red - solvent velocity profile, black - polymer density profile, green - probability density of finding nanoparticle at a particular distance from the wall

COLL 100

Fouling behavior of chemically modified mixed liquor from submerged ceramic biofilm-membrane bioreactor

Zakhar Maletskyi, zakhar.maletskyi@nmbu.no, Olga Kulesha. Faculty of Science & Technology, Norwegian University of Life Sciences, Aas, Norway

Wastewater treatment with membrane bioreactor has a number of advantages over conventional technologies: excellent nutrient removal efficiency, compactness, complete biomass retention without a secondary clarifier and low carbon footprint. Stringing environmental regulations and shift to the circular economy drive expansion of the global MBR market to 8.27 USD billion by 2025. Membrane fouling, causing high operating costs and rising the need in skilled technical support, remains being the main restraint to further penetration of MBR into cost-sensitive markets. BioFilm Membrane BioReactor (BF-MBR) comprises well-proven practical advantages of both biofilm and MBR treatment processes, but the range of stable operation conditions can be

significantly narrowed due to strong mechanical interactions between biofilm carriers and suspended sludge under intensive aeration-mixing, leading to disintegration of sludge flocks and formation of smaller charged particles.

This study compares coagulants as Membrane Fouling Reducers (MFRs) based on results of Total Recycle Tests (TRTs) and characteristics of coagulant-treated sludge by means of particle size distribution (PSD), electrokinetic potential (ζ -potential) and Capillary Suction Time (CST).

The obtained results show that dosing of aluminium and iron containing coagulants to mixed liquor of BF-MBR leads to considerable increase of filtration time by predominantly affecting electrokinetic potential of sludge particles: from 2.4-11 min for raw ML to 32.1-103.5 min at 0.11-1.96 $\mu\text{mol-Me/mg-SS}$ of MFR.

It is demonstrated that dosing of aluminium and iron containing coagulants as membrane flux enhancers to mixed liquor of BF-MBR compensates electrokinetic potential of sludge particles and subsequently alleviates membrane fouling, increasing filtration time by 3-43 times, depending on reagent type and application conditions. Pre-polymerized aluminium chloride hydroxide shows the best result at dose ten times lower than coagulation dose in conventional wastewater treatment processes.

COLL 101

Effect of inorganic salt as porogen on the structure and properties of polyvinylidene fluoride(PVDF) membranes

Ming Zhang, zm2404@tjut.edu.cn, Yue Song. School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, China

This study explored the impact of inorganic salts (NaCl, KCl, LiCl) as an inorganic additive in the preparation of polyvinylidene fluoride (PVDF) membranes using the phase inversion technique. PVDF membrane were prepared by varying the percentage of inorganic salts (NaCl, KCl, LiCl)(0-5wt%) in the dope solution. The dimethyl acetamide(DMAc) was used as the solvent of dope. The inorganic salts were dissolved in deionized water, and then added into the PVDF/DMAc dope solution. The experimental results showed that the contact angle decreased as inorganic salts were added in the casting solution. With the increasing concentration of NaCl, KCl, LiCl from 0-5wt%, the water flux increased from 60L/m²h to 980 L/m²h and the rejection decreased from 90.0% to 55.0%, meanwhile, the static contact angle stabilized basically around 70°. The membrane were characterized through scanning electron microscope(SEM), transmission electron microscope(TEM) and Brunauer-Emmett-Teller(BET), respectively. The results indicate that the inorganic salt are uniformly dispersed in PVDF membranes, the pore structure showed obvious change as the amount of inorganic salt.

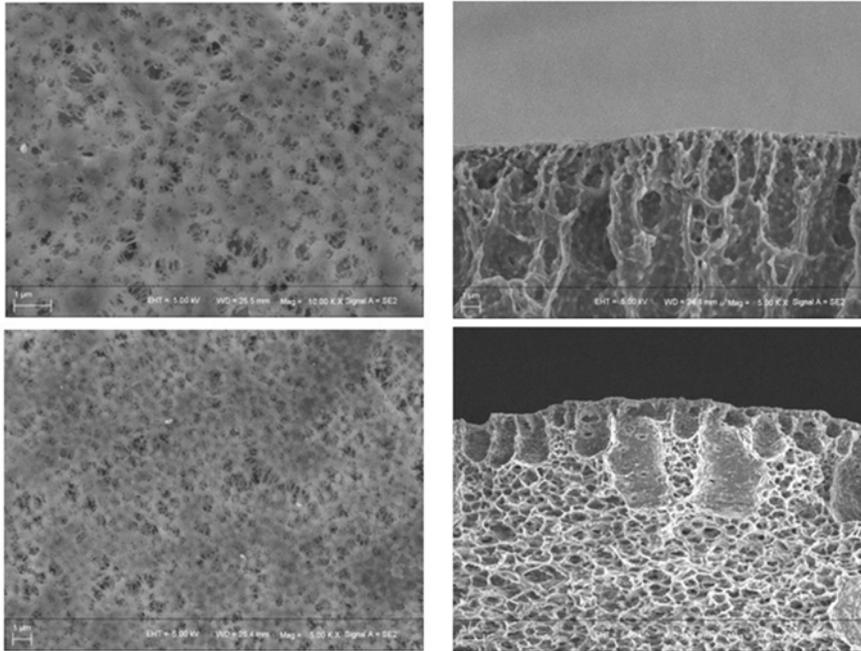


Figure1 SEM images of PVDF membranes with different amount of NaCl additive

COLL 102

Synthesis and catalytic applications of Ru nanocrystals with well-controlled facets and an fcc structure

Younan Xia, younan.xia@bme.gatech.edu. Molecular Science Engineering Building, Georgia Institute of Technology, Atlanta, Georgia, United States

Catalysts based on Ru nanocrystals have received great interest because of their great performance in an array of applications, including ammonia synthesis, Fischer-Tropsch synthesis, and CO oxidation. In addition to those with the conventional hexagonal-close packed (hcp) structure, Ru nanocrystals with a face-centered cubic (fcc) structure has recently emerged as an active subject of research. In this talk, I will discuss our recent successful syntheses of Ru nanocages enclosed by different types of facets (including twin boundaries), together with an fcc crystal structure. Based on in situ XRD, the fcc structure could be retained up to a temperature as high as 300 °C. We have also evaluated the facet-dependent catalytic properties of the fcc-Ru nanocages toward a number of model reactions, including the reduction of 4-nitrophenol and decomposition of hydrazine, as well as ammonia synthesis.

COLL 103

Crystal phase-engineering of novel nanomaterials

Hua Zhang, *hzhang@ntu.edu.sg*. School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

In this talk, I will summarize the recent research on the crystal phase engineering of nanomaterials in my group. It includes the first-time synthesis of hexagonal-close packed (*hcp*) Au nanosheets (AuSSs) on graphene oxide, surface-induced phase transformation of AuSSs from *hcp* to face-centered cubic (*fcc*) structures, alternating *hcp/fcc* Au square-like plates from AuSSs, ultrathin Au nanowires containing *hcp* phase, synthesis of ultrathin *fcc* Au@Pt and Au@Pd rhombic nanoplates through the epitaxial growth of Pt and Pd on the *hcp* AuSSs, respectively, the first-time synthesis of 4H hexagonal phase Au nanoribbons (NRBs) and their phase transformation to *fcc* Au RNBs, the epitaxial growth of Ag, Pt, Pd, PtAg, PdAg, PtPdAg, Rh, Ir, Ru, Os and Cu on 4H Au NRBs to form the 4H/*fcc*Au@metal core-shell NRBs, and the synthesis of 4H/*fcc*-Au@metal sulfide core-shell NRB heterostructures. In addition, the crystal phase transformation of transition metal dichalcogenide nanomaterials will also be introduced. Currently, my group focuses on the crystal phase-based properties and applications in catalysis, surface enhanced Raman scattering, waveguide, photothermal therapy, chemical and biosensing, etc., which we believe are unique and critically important not only fundamentally, but also practically. Importantly, the concept of crystal phase heterostructures of nanomaterials is proposed.

COLL 104

Coordination assemblies of nanoparticles

Nicholas Kotov, *kotov@umich.edu*, Zhi-Bei Qu, Weijie Feng, Yichun Wang, Kenji Hirai. University of Michigan, Ann Arbor, Michigan, United States

Assembly of inorganic nanoparticles (NPs) into higher order constructs is typically driven by non-covalent interactions that include electrostatic, van-der-Waals, hydrophobic forces, volume exclusion interactions⁴, and hydrogen bonds. Assemblies of NPs and nanocarbons into organized superstructures driven by coordination bonds are hardly known although they can potentially display a remarkable variety of functionalities even for fairly simple organizational motifs such as chains, sheets, and shells. The limited knowledge about such assemblies is particularly conspicuous because there is a large number of self-assembled complexes and solids constructed from small molecules using coordination bonds. Hybridization of electronic and magnetic states of inorganic nanostructures with those of coordination compounds complemented by different assembly pattern provides a powerful toolbox for novel catalytic, optical, and electronic materials.

In this talk we shall demonstrate the possibility to form spontaneous assemblies of NPs due to coordination bonds between them and their utilization for electrocatalysis in organic media. Coordination assemblies of discotic NPs result in marked reduction of overpotential. Furthermore, coordination assemblies have connotations for the Earth's sciences. Nanoscale metal oxides, sulfides, silicates, and carbon are abundant in the Earth's water and so, are metal ions, which leads to distinct possibility of their formation

in various natural environments. Limited knowledge of nanoscale assemblies in the context of geological and environmental processes provides a compelling reason for investigation of coordination assemblies of NPs and nanocarbons.

COLL 105

Atomically precise metal nanoparticles and their assembly

Rongchao Jin, *rongchao@andrew.cmu.edu*. Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Assembly of nanoparticles (NPs) into complex architectures across length scales is of paramount importance in nanoscience and nanotechnology, especially for various applications. Despite the major advances, NP assembly has not achieved atomic-level understanding yet. Recent progress in nanochemistry has led to atomically precise nanoparticles (e.g. gold) with their total structures (i.e., metal core plus surface ligands) fully determined by X-ray crystallography. Such unique nanoparticles provide an opportunity for understanding NP assembly mechanisms at unprecedented levels. This talk will present several case studies. The precise structural information across the Ångström to macro scale reveals that the protecting ligands can generate complex patterns on the NP surface, and that the symmetry and density of the surface patterns further guide the packing of NPs into lattices with orientational, rotational, and translational order.

COLL 106

Probing the atomic arrangement of palladium on silver nanocrystals with an isocyanide-based reporter by surface-enhanced Raman scattering

Dong Qin, *dong.qin@mse.gatech.edu*, **Yiren Wu**. Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

We report the use of 2,6-dimethylphenyl isocyanide (2,6-DMPI) as a molecular probe for characterizing the overgrowth of Pd on Ag nanocubes using surface-enhanced Raman scattering (SERS). When 2,6-DMPI binds to Ag *via* σ^* donation from σ^* orbitals of isocyanide to *d*-band of Ag, the stretching frequency for the NC bond, ν_{NC} , shows a blue shift. In comparison, when 2,6-DMPI binds to Pd *via* π -back donation from *d*-band of Pd to the π^* antibonding orbital of isocyanide, the ν_{NC} band exhibits a red shift. More significantly, the isocyanide group could anchor to Pd atoms in an atop, bridge, or hollow configuration with a continuous red shift in ν_{NC} , making it possible to resolve the atomic structures of Pd on the surface of Ag nanocubes during the overgrowth. We also demonstrate the possibility of directly introducing 2,6-DMPI to the original growth solution for *in situ* monitoring the real-time atomic arrangements of Pd during the overgrowth in the liquid phase and under ambient condition. The change in ν_{NC} could provide detailed information for the reduction, deposition, and diffusion process as the overgrowth progresses. With atomic sensitivity, this *in situ* method could shed light on

the mechanistic details in the seeded overgrowth. This work would support the rational design of bimetallic nanocrystals with other noble metals like Pt, Rh, Ir, and Ru.

COLL 107

Towards precision catalysts through the control of bimetallic nanostructures

Hong Yang, *hy66@illinois.edu. Chem. Biomol. Engr., Box C-3, MC-712, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States*

Many important chemical transformations involve the use of nanoparticles as catalysts, and the ability of controlling nanostructures is central for a range of sustainable applications, ranging from fuel cell and battery to CO₂ utilization. Thus, it is essential to control the nanostructures that are important to catalysis, that is, the surface atomic structures and their dynamics under the reaction environments. In this presentation, I will discuss our recent efforts towards addressing the challenges in the precision control of structural variables of metal catalysts and provide our understandings on the factors governing the restructuring process of bimetallic nanocatalysts, ranging from diffusion to thermodynamics of bulk and surface energetics. In situ environmental transmission electron microscopy (ETEM) is used to determine the factors affecting the dynamics of near surface structures. Such information is used for the post-synthesis processing of bimetallic nanocatalyst for improved performance, which was demonstrated in the thermally driven composition redistribution of Pt-Ni octahedral oxygen reduction reaction (ORR) catalyst, and the adsorbate-assisted regioselective atomic rearrangement of catalysts. Our data show how multiple governing factors determine the restructuring of bimetallic catalysts under reactive thermal-chemical environments. Such information provides insights in the synthesis and processing of bimetallic catalysts, and on the design of reaction conditions for the high performance.

COLL 108

LeChatelier on the nanoscale

Catherine J. Murphy, *murphycj@illinois.edu. Box 59-6, Univ of Illinois at Urbana-Champaign, Urbana, Illinois, United States*

Photothermal heating using plasmonic nanoparticles takes advantage of the particles' near-infrared absorption of light to generate heat. Many groups have used this phenomenon to their advantage for light-triggered delivery of drugs or other molecules. However, this process only works if the binding of the small molecule to the nanoparticle is exothermic in nature ($A + B \rightarrow AB + \text{heat}$); upon heating, the "AB" complex should dissociate into its constituents. An endothermic association, then, should adsorb MORE molecules to the plasmonic nanoparticle upon photothermal heating. In this talk I will demonstrate our recent results that indeed show that LeChatelier's principle works for various protein/nanoparticle systems.

COLL 109

Controlling biomolecular corona by plasmonic metal nanoparticles

Ester Polo, ester.polo@usc.es. Ciqus, University Santiago de Compostela, Santiago de Compostela, Coruña, Spain

Engineered materials in the nanoscale are revolutionizing all areas of life science, thanks to their novel physicochemical properties. There are many different aspects that need to be considered when designing nanomaterials for *in vivo* targeting. The dispersion size and stability, possible non – specific interactions and targeting capabilities all need to be well understood and controlled. However, it becomes crucial to know how an engineered nanomaterial acts when inside a biological system. The interaction of nanoparticles with the biological environment results in the formation of a biomolecular corona, which substantially modifies the nanoparticle surface properties, and ultimately mediates the interactions of nanoparticles with cells and organisms. It has been shown that the material, size and shape of a nanoparticle all affect the composition of the formed corona. The composition and architecture of the biomolecules on their surface in turn affect the bio-interactions and thus *in vivo* nanomaterial destination.

By using the physicochemical properties of inorganic nanoparticles, such as plasmonic heating, allow us to control the corona composition, the long-lived protein coating, as well as the exposure of certain protein domains on the nanoparticle surface that could lead to different nanomaterial destination and trigger specific cellular responses.

COLL 110

Low-dose exposure of graphene oxide significantly increases metal toxicity to macrophages by altering their cellular priming state

JianQiang Zhu¹, zjqwfm@126.com, Sijin Liu². (1) State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Beijing, China (2) Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

Given the novel physicochemical properties, graphene materials, such as graphene oxide (GO), are being developed for applications in various fields including biomedicine. Nonetheless, considerable knowledge gaps still exist regarding the understandings on GO's environmental health and safety (EHS) impacts. Thus far, little attention has been paid to its secondary toxicity, synergistic effects and mal-adaption. Here, we show that GO at low concentrations (that did not directly incur significant cytotoxicity) can greatly enhance metal toxicity in macrophages by altering their cellular priming state. Specifically, GO caused impairments to cellular morphology and membrane integrity in macrophages, and remarkably enhanced cellular uptake of cadmium (Cd) and other non-essential metal ions (e.g. Hg and Gd). Furthermore, upon low-dose GO pre-

treatment Cd at a non-toxic concentration brought about marked oxidative stress in macrophages and ultimately increased cell death. Mechanistic investigation illustrated that GO pre-treatment triggered cell death through apoptosis under Cd exposure. Overall, this study opens a new path to understand GO's EHS impacts through a perspective of synergistic and secondary effects, a previously unidentified mechanism via which nanomaterials may pose detrimental effects on organisms.

COLL 111

Magnetite nano-clusters for biomedical magnetic nanoparticles fluid hyperthermia for cancer treatment

David Quesada¹, dquesada@stu.edu, Luis C. Fernandez¹, Alexis Tapanes-Castillo¹, Maria Barreat^{2,1}. (1) St. Thomas University, Miami Gardens, Florida, United States (2) University of Miami, Coral Gables, Florida, United States

Magnetic Nanoparticles Fluid Hyperthermia is called to be a promising treatment method for cancer lesions, constituting an alternative pathway to other medical approaches, as for example, chemotherapy and radiotherapy. Even though, this method is not the total cure for cancer, it is choice in cases of very aggressive evolution, when patient and doctors need to buy time and maintain the patient in good medical conditions. The large surface area to volume ratio of nanoparticles makes them a suitable element to amplify the effect of external fields, in particular, the heat generated by alternating magnetic fields. Despite of these promising possibilities, a critical problem of hyperthermia is the direct control of the heat source and the distribution of nanoparticles in order to induce necrosis within cancerous cells with the minimum negative impact to the surrounding healthy cells. In this presentation, magnetite Nano clusters are obtained through a precipitation method and functionalized such that they might stick to a line of breast cancer cells. A laboratory set up using Helmholtz coils is used to generate a homogeneous magnetic field, in which samples with different concentrations of magnetite Nano clusters are placed. Samples are analyzed before and after the magnetic field is activated. Moreover, a biomedical modeling of the process of hyperthermia is carried on for cancer cells of different geometries appealing to the modified Penne's bioheat equation and the Finite Element Method (FEM). Special attention was paid to the size and spatial distribution of nanoparticles. The results from numerical solutions have permitted to establish guidance towards optimal conditions for its use. Computations were performed in Wolfram Mathematica

COLL 112

Vortex state in magnetite nanodiscs: A foundation for multimodal mechanothermal neuronal stimulation

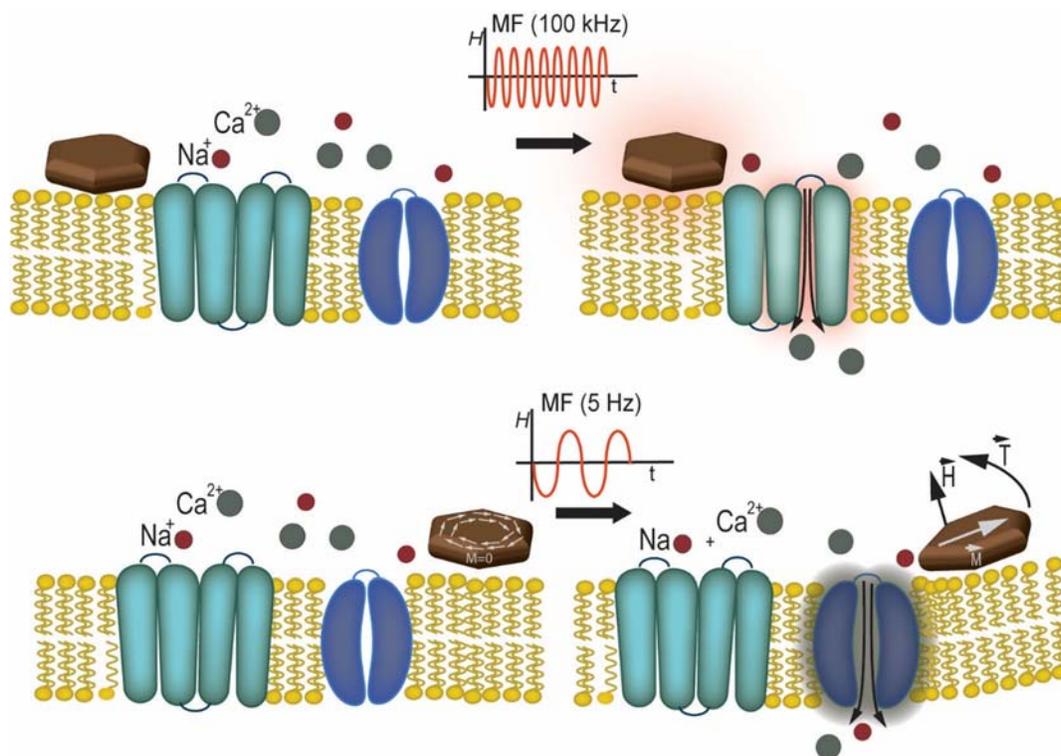
Gregurec Danijela¹, gregurec@mit.edu, Alexander W. Senko², Andrey Chuvilin³, Pooja Reddy², Ashwin Sankararaman², Dekel Rosenfeld², Francisco Garcia², Junsang Moon², Po-Han Chiang², Polina Anikeeva². (1) RLE, Massachusetts Institute of Technology,

Cambridge, Massachusetts, United States (2) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) Electron Microscopy Laboratory, CIC Nanogune, San Sebastian, Spain

Wireless schemes based on hysteretic heating of magnetic isotropic nanoparticles in high-frequency alternating magnetic fields (AMFs) have already permitted modulation of neural activity. We present a novel approach for neuronal modulation based on magnetite nanodiscs (MNDs). These anisotropic iron oxide nanomaterials exhibit a characteristic vortex alignment of magnetic spin with zero net magnetization in the absence of external magnetic field. Such magnetic configuration fosters the colloidal stability in physiological solutions essential for applications in biomedicine. We synthesize a geometric palette of MNDs from 40 nm to 250 nm in diameter. Consistent with geometry, MNDs exhibit direction-dependent hysteresis loops and their specific loss power (SLP) at frequencies of 75-150 kHz up to 1000 W/g is comparable to the spherical magnetite nanoparticles, but at 5-10 times lower particle count owing it to the size of MNDs. Targeted activation of heat gated channels is thus permitted at high frequency AMFs.

Furthermore, the magnetization in the presence of weak magnetic fields assumes an “in-plane” orientation revealing a large magnetic moment that allows MNDs to transduce magnetic fields to mechanical torques at slow-varying magnetic fields. We show how the mechanical torques are further transduced to the mechanical stimuli of neuronal cells. These stable, biocompatible MNDs robustly mediate calcium influx in mechanosensitive sensory neurons from rat dorsal root ganglia (DRGs) upon application of weak (23 mT), slow-varying (1-5 Hz) magnetic fields.

Finally, MNDs allow for multiplexed stimulation of neurons by selectively activating mechanoreceptors at 1-5 Hz magnetic fields, while heat dissipation and consequent activation of heat-gated ion channels is allowed at frequencies of around 100 kHz.



Principle of multimodal neuronal stimulation with magnetite nanodiscs; Magnetothermal activation of heat gated ion channels at high frequency (top) and activation of mechanoreceptors by torque at low frequencies (bottom).

COLL 113

Biotransformation of graphene oxide in lung fluids significantly alters its inherent properties and bioactivities towards immune cells

Sijin Liu, sjliu@rcees.ac.cn. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

Engineered nanomaterials (such as graphene oxide, GO) have shown great potential in biomedical applications as therapeutic and imaging agents. However, little is known about their potential transformation in biological settings that may alter their physicochemical properties and consequently, may hinder their biomedical applications. Here, we show that GO undergoes significant physicochemical transformation in two simulated human lung fluids – Gamble’s solution and artificial lysosomal fluid (ALF), as the organic acids (e.g., citrate and acetate) in lung fluids cause reduction of GO, mainly due to the conversion of epoxy and carbonyl to phenolic groups. Biotransformation markedly inhibits the endocytosis of GO by scavenging macrophages. Notably, alterations in Gamble’s solution enhance the aggregation of GO in a layer-to-layer manner, resulting in GO precipitation and reduced interaction with cells, whereas changes in ALF lead to edge-to-edge aggregation of GO, enhancing the adhesion of

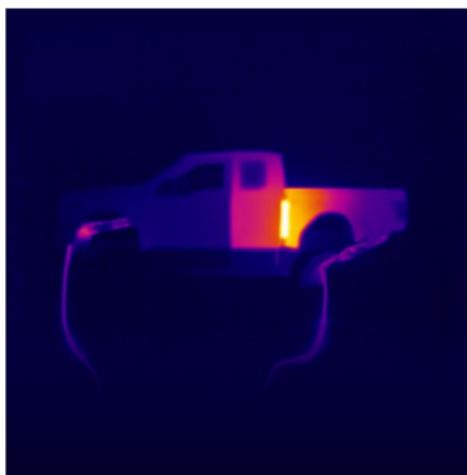
large sheet-like GO aggregates on plasma membrane without cellular uptake. The varied interaction mechanisms towards macrophages eventually induce differential pro-inflammatory reactions. Experiments conducted in mice corroborated morphological alterations of GO in realistic lung microenvironment. Overall, the findings suggest that biotransformation of nanomaterials may significantly alter their inherent properties, and therefore, affect their biosafety such as the clearance of “worn-out” nanomaterials by immune cells, giving rise to potentially long-term side effects at the accumulating sites.

COLL 114

Radio frequency heating of carbon nanotube loaded materials

Micah J. Green¹, micah.green@tamu.edu, **Charles Sweeney**¹, **Mohammad Saed**². (1) *Chemical Engineering, Texas A&M University, College Station, Texas, United States* (2) *Electrical & Computer Engineering, Texas Tech University, Lubbock, Texas, United States*

We show the RF electromagnetic heating of carbon nanotubes (CNTs) in a dielectric matrices via direct contact and capacitively-coupled electric field applicators in the 1-200 MHz region; prior reports had noted CNTs’ strong microwave heating response, but this is the first report of RF electric fields rapidly heating these materials. We highlight our novel RF heating technique for multi-walled carbon nanotube (MWCNT)/polymer composites and measure their broadband dielectric properties. We also demonstrate three different electric field applicator configurations and discuss their functional applications. We demonstrate the use of RF heating to cure epoxy loaded with MWCNTs and weld conductive structures together. Our results show that lap shear joints cured faster with the RF method compared to control samples cured in an oven due to the heat transfer advantages of directly heating the epoxy composite. This method allows for volumetric, rapid heating in a variety of dielectric matrices, with potential applications in thermal imaging, nanotube detection, and ablation.

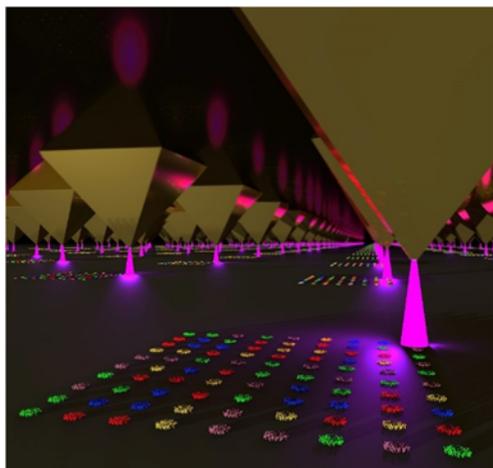


COLL 115

Molecular printing: Combining organic chemistry and nanolithography to recreate biointerfaces

Adam B. Braunschweig^{1,2}, adam.braunschweig@asrc.cuny.edu. (1) *Advanced Science Research Center, City University of New York, New York, New York, United States* (2) *Department of Chemistry, Hunter College, New York, New York, United States*

Multiplexed microarrays – where different biological probes are spatially encoded onto a surface into spots with micrometer-scale diameters – have facilitated the rapid advancement of “Omics” research. Further miniaturization of feature diameters could increase the number of probes in a microarray, reduce sample required for analysis, and result in surfaces with the chemical and topological complexity of natural biological interfaces. Tip-based lithography (TBL) has gained popularity for patterning delicate, biologically-active materials, but no versatile TBL-based multiplexing strategy, where different molecules are patterned in close proximity, has been devised. Doing so requires synergistic advances in nanolithography and surface organic chemistry. Here we use massively parallel tip-based lithography to induce thermally, photochemically, and mechanically-activated organic surface reactions. Subsequently, the combination of microfluidics, beam pen lithography, and photochemical surface reactions to create multiplexed arrays will be discussed. For proof-of-concept, the thiol-ene reaction was optimized, and the reaction kinetics were analyzed to produce a series of patterns intended to demonstrate the power and versatility of this new printing approach. This patterning strategy is a powerful approach for studying and optimizing organic reactions on surfaces and creating massively multiplexed arrays, and, as such, could provide an entirely new approach for miniaturizing biochips or understanding interfacial reactivity.



COLL 116

Directed assembly for three-dimensional nanoprinting

Gang-Yu Liu¹, *gail.panda@gmail.com*, **Shuo Wang**¹, **Joao Francisco Ventrice de Souza**², **Yang Liu**³, **Tonya Kuhl**⁴, **Pablo Doerig**⁶, *pablo.doerig@cytosurge.com*, **Jane Frommer**⁵. (1) Dept Chemistry, Univ of California, Davis, California, United States (2) Chemistry, University of California, Davis, California, United States (3) Department of Chemistry, University of California, Davis, Davis, California, United States (4) Dept. Chemical Engineering and Materials Science, University of California Davis, Davis, California, United States (5) IBM Almaden Research Center, San Jose, California, United States (6) Cytosurge LLC, 8152 Glatthbrugg, Sägereistrasse 25, Switzerland

Directed assembly are a generic and simple means to produce designed structures in three-dimensions (3D). The printing is achieved by extruding printing materials through a nozzle, which provides a platform to deliver a wide range of materials. Although this method has been routinely used for 3D printing at macroscopic scales, miniaturization to micrometer and nanometer scales and building hierarchical structures at multidimensional scales represent new challenges in research and development. This presentations addresses these challenges by combining the spatial precision of atomic force microscopy (AFM) and local delivery capability of microfluidics. Specialized AFM probes serve dual roles of a microscopy tip and a delivery tool, enabling the miniaturization of 3D printing *via* direct material delivery. Various designed 3D structures of chosen materials were produced, whose spatial precision is among the highest in 3D printing. The results clearly demonstrate the feasibility of achieving 3D nanoprinting with nanometer feature size and accuracy with practical throughput and overall size. This work paves the way for advanced applications of 3D hierarchical nanostructures.

COLL 117

Integration of colloidal giant quantum dots and 3D nanoantennas by dip-pen nanolithography

Jun Wang¹, *junwang.nano@gmail.com*, **Farah Dawood**¹, **Peter Schulze**¹, **Chris Sheehan**¹, **Isabelle Staude**^{3,4}, **Igal Brener**³, **Nabil A. Amro**², **Jennifer A. Hollingsworth**¹. (1) Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Advanced Creative Solutions Technology LLC, Carlsbad, California, United States (3) Sandia National Laboratories, Albuquerque, New Mexico, United States (4) The Australian National University, Canberra, Australian Capital Territory, Australia

Colloidal semiconducting nanocrystals, or quantum dots (QDs), when coupled to subwavelength nanophotonic structures, such as optical nanoantenna and nanoscale resonators, can have enhanced emission properties – enhancement of the radiative rate by the well-known Purcell effect, improved excitation efficiency, and control over the direction and polarization of emitted light. Here, we report the integration by dip-pen nanolithography (DPN) of ultra-photostable giant QDs (gQDs) and three-dimensional nanoantennas as a prototype hybrid system for realizing such enhanced light-emission properties. DPN is a scanning probe-based alternative lithography technique that uses an atomic force microscope tip to precisely “write” liquid “ink” onto diverse solid

substrates. We report a comprehensive investigation of factors controlling DPN of complex liquid inks comprising a non-aqueous carrier solvent and suspended gQDs. Two different sized gQDs were used, and with different colloidal stability of the suspension, a very different DPN inking/writing behavior was observed. We also studied key DPN experimental parameters and their relationship to deposition rate, including dwell time, surface-ink interactions (surface hydrophilicity/phobicity effects) and volume of ink on the writing tip. We further advanced a three-step reading-inking-writing approach using DPN to precisely place gQDs onto the nanoantennas, realizing for the first time deposition targeted to sub-micron substrate features. Overall, the new understanding of ink-substrate interactions and the parameters controlling bulk fluid flow from nano-tip to substrate lays the groundwork for the expanded use of DPN for integration of multi-component nanostructures, comprising “soft” and “hard” constituents, that would be challenging or impossible to create using traditional lithographic techniques.

COLL 118

Direct assembly of hydrophobic quantum dots with colloidal silica via van der Waals interaction

Kyoungja Woo, kjwoo@kist.re.kr, Hyein Yoo. Korea Institute of Science and Technology, Seoul, Korea (the Republic of)

Various approaches have been reported for hybridization of silica colloids and quantum dot (QD) nanocrystals due to their useful applications in many fields, such as light emitting diode, display, bio-imaging, and sensing, etc. Most of the approaches require a ligand exchange process of the as-prepared nanocrystals which is hydrophobic due to the protecting ligands, before or during their hybridization. The ligand exchange process frequently brings about a complicated situation, such as aggregation of nanocrystals or optical deterioration. A direct assembly without the ligand exchange process can be greatly prospective, but has been challenging.

A weak physical interaction, the van der Waals (vdW) force has been considered incapable of making a stable assembly of two different hydrophobic colloidal particles. They can be associated and dissociated reversibly. However, in a nanoscale regime, the reinforced vdW force due to an enlarged contact area can have a substantial impact. To prove it, we prepared hydrophobic colloidal silica (S° , $\sim 114 \pm 11$ nm) from tetraethoxysilane and octadecyltrimethoxysilane (TEOS and ODTMS) mixture precursors. The S° is constructed by controlled aggregation of 15~25 nm-sized hydrophobic silica particles and thus, has many crevices where the QDs can sit on. The hybridization works nicely as long as the QD size fits within the concave regions of OD-silica. The hybridized structure is securely covered by silica with/without functional groups and exhibits greatly enhanced photoluminescence (up to 690%) than their free QDs under an identical QD concentration. The current approach was successfully extended to three different sized QD nanocrystals (≤ 10 nm). To the authors' knowledge, this is the first report showing versatile hybridization of hydrophobic

nanocrystals with colloidal silica using the vdW force only. A brief application for a white LED is also provided, with a promising optical performance.

COLL 119

Ligand-mediated structural transformations in PbS nanocrystal superlattices

Samuel W. Winslow¹, swinslow@mit.edu, **Detlef Smilgies**², **James Swan**³, **William A. Tisdale**¹. (1) *Chemical Engineering, MIT, Cambridge, Massachusetts, United States* (2) *Cornell University, Ithaca, New York, United States*

Understanding the temperature-dependent transformations of nanocrystal solids is critical to interpretation of temperature-dependent charge transport measurements and can inform our understanding of self-assembly processes. Using Grazing Incidence Small- and Wide-Angle X-ray Scattering (GISAXS and GIWAXS) and GPU-accelerated coarse-grained molecular dynamics simulations, we studied the distortion of colloidal PbS nanocrystal superlattices between room temperature and cryogenic temperatures. Experimental data show that, regardless of the nanocrystal size or dispersity, the superlattice reversibly distorts by contracting along one axis and expanding along two axes. Interestingly, hysteresis in the pathway is observed and attributed to a ligand order/disorder transition, which presents a thermodynamic barrier upon cooling which is absent during heating. These results reveal the central importance of the ligands and solvent in dictating superlattice structure upon cooling. This fundamental understanding also serves as a potential route for engineering chosen lattice polymorphs at a specific temperature.

COLL 120

Long range hierarchical assembly of Pt nanocrystals – Insights from measurements and molecular simulations of nanoparticle docking

Shiyi Wang¹, shwa7968@colorado.edu, **Enbo Zhu**², **Xucheng Yan**², **Masoud Sobani**³, **Lingyan Ruan**², **Chen Wang**², **Yuan Liu**², **Xiangfeng Duan**^{4,5}, **Hendrik Heinz**¹, **Yu Huang**^{6,5}. (1) *Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States* (2) *Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, California, United States* (3) *Department of Polymer Engineering, University of Akron, Akron, Ohio, United States* (4) *Dept of Chemistry, Univ of California, Los Angeles, California, United States* (5) *California NanoSystems Institute, University of California, Los Angeles, California, United States* (6) *Dept of Material Sci Engr, UCLA, Los Angeles, California, United States*

The hierarchical control of biogenic minerals from the morphology at the nanometer scale to subsequent assembly into macroscopic structures remains a major challenge. Although considerable efforts have been devoted to exploring effects of biomolecules in the biomineralization process, the studies to date are largely limited to atomic/molecular

scale crystallization. Here it is shown how higher order structures of biomolecules exert critical effects on the long range assembly of biominerals for the example of platinum nanocubes aligned in 1D and 2D patterns. A Pt{100} specific peptide T7 (Ac-TLTTLTN-CONH₂) adopts ST-turn conformations at low concentration in solution that supports the formation of cubic Pt nanocrystals and then spontaneously transforms these structures into β -sheets with increasing concentration. During this molecular assembly process the T7-Pt{100} specific interaction drives cubic Pt nanocrystal into large area and long range linear assembly along the [100] direction. We discuss the analysis of interactions between individual peptides to form long-range ordered structures in atomic-level detail by molecular dynamics simulation and their directional preferences of interaction with Pt nanocubes. The interaction energy with Pt (100) surfaces and facets is larger when peptide strands are parallel to the surface with side chains oriented flat-on to the surface rather than perpendicular. It is also found that docking of the Pt nanoparticles into 1D assemblies typically involves a 1.2 nm thick interlayer of water and a single T7 peptide in quasi ST-turn structure sandwiched between the nanoparticles. It is shown how small free energy differences on the scale a few kcal/mol support the observed directional assembly, help propose a mechanism to explain the formation of 1D and 2D ordered structures, and the reversibility of the process by changes in temperature or concentration. The findings, especially on the experimental side, mark a critical milestone in biomimetic material synthesis, and open vast opportunities for materials engineering with programmable structures from the atomic scale to the macroscopic scale.

COLL 121

Fabrication of hierarchically ordered optically active nanocrystal solids by surface passivation using atomic layer deposition of metal oxides

Riya Bose¹, riyabose87@gmail.com, Aaron Dangerfield², Sara Rupich², Yves J. Chabal², Anton Malko². (1) Department of Physics, University of Texas at Dallas, Richardson, Texas, United States (2) University of Texas at Dallas, Richardson, Texas, United States

In order to improve solar energy harvesting, several types of architectures and active materials have been suggested for photovoltaic devices that may surpass the Shockley-Queisser limit for single p-n junction solar cells. Nanostructured energy transfer (ET) hybrids involving quantum dots (QDs) in conjunction with Si substrate provides an attractive alternative, as excitonic energy transfer and sensitization of Si layer by spectrally tunable quantum dots with high absorption coefficient eliminates the weak absorption factor in indirect bandgap Si, whereas the high carrier mobility Si component can be used for charge separation and transport. Use of a multilayer of differently sized quantum dots may further enhance the efficiency of the device by increasing the spectral absorption window. However, one of the difficulties in fabrication of multilayer QD films remains with the solution phase deposition method, where the application of the solvent in each of the subsequent deposition steps may affect the morphology of the previous layer. Further, surface passivation techniques play a critical role to protect the

deposited QD layers from oxidation and deterioration during long-term use. An attractive method to passivate QD films is to overcoat them with various metal oxides grown using atomic layer deposition (ALD). Although there are a few reports of ALD encapsulation of QD films, they mostly concentrate on QDs with short ligands designed for charge transfer based devices, and report significant quenching of the photoluminescence (PL) intensity. However, for an efficient ET based multilayered QD/Si photovoltaic devices, preservation of the PL is necessary. In this study, we investigate the exact growth mechanism of metal oxides by ALD on the surface of quantum dots and its influence on PL properties. We start with well-developed QD systems like CdSe/ZnS core-shell nanocrystals and Al₂O₃/ZnO as the metal oxide layers. We investigate interaction of the ALD precursors with the QD surface ligands by using in-situ FTIR and ex-situ XPS measurements along with the time-resolved QD PL lifetime measurements to evaluate the extent of emission quenching. Our measurements indicate the importance of ALD parameters as well as the length and composition of the passivating ligands on the resulting PL of QD films. This approach is currently being applied to create dense QD solids using new generation of multiexciton-bearing QDs of various dimensionalities and compositions.

COLL 122

Directed assembly and nano-soldering of multi-segment metallic nanowires

Jirui Wang¹, jirui_wang@student.uml.edu, Fan Gao¹, Chefu Su², Junwei Su², Hongwei Sun², Zhiyong Gu¹. (1) Chemical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States (2) Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States

Although the rapid growth of nanotechnology has brought enormous opportunities for new nanomaterials (such as nanowires, carbon nanotubes, or graphene) and a wide range of potential applications in electronics, photonics, sensors, and energy conversion and storage devices, there are still several critical issues blocking the way for widespread manufacturing of electronics and devices. One of the most challenging problems is how to form effective interconnects between nanocomponents, which will affect device performance and reliability. In this work, multi-segment nanowires with a magnetic core in the middle and two soldering ends were successfully synthesized through a template assisted electrodeposition method and then applied for assembly and soldering. The nanowire fabrication process included using different electrolytes to enable the electrodeposition in sequence, and the length of each segment was controlled by different current density and deposition time. 2D micro-patterns on Si/SiO₂ substrate were fabricated by lithography, and multi-segment nanowires were then connected into 2D or 3D structures by magnetic-assisted self-assembly method. After that, aligned multi-segmented nanowires were soldered and joined together by IR soldering. The IR soldering is a localized heating method and can be used as a new soldering method to overcome some challenging issues, where the conventional soldering methods such as resistance heating, soldering iron melting and oven heating may not be applied to. The results from this research give us a better understanding of

magnetic assisted assembly and IR soldering design of nanocomponents for nanodevices and nanoelectronics. These ordered 2D or 3D structures formed by self-assembly and nano-soldering can be used for various applications such as nanoelectronics, nanosensors, energy conversion, harvesting and storage.

COLL 123

Self-assembly of spatially-decorated metallic nanowires on a fluid interface

Guillaume Staelens, guillaume.staelens@uclouvain.be, Alain M. Jonas, Bernard Nysten, Sophie Demoustier-Champagne. IMCN/BSMA, Universite Catholique de Louvain, Louvain-la-Neuve, Belgium

Films of metallic nanowires are of interest for the fabrication of optical filters; when assembled on a fluid interface and grafted by stimuli-responsive moieties, they could exhibit on-demand reconfigurability, thereby providing access to stimuli-tunable filters. Here, we explore the assembly over water of Pt and Au nanowires decorated at specific locations by chemical functions which can be modified by pH stimuli. The nanowires are synthesized by electrochemical deposition in nanoporous membranes, typically polycarbonate membranes, leading to nanowires of controlled diameter, length and composition. This templating methodology simultaneously allows us to modify specific parts of the nanowire surface such as their bases or lateral face [see Figure 1] with a wide range of chemical functions, using either thiol assembly or polyelectrolyte adsorption. Then, the spatially-decorated nanowires are assembled in a film at the oil/water or air/water fluid interface, and can be transferred to a solid substrate for characterization. We discuss the assembly of the nanowires in films of varying degrees of order, depending on their assembly method and on their spatial functionalization. One of the key parameters in the assembly is the type of chemical functions grafted on the nanowires, which can control ordering while avoiding 3D aggregation when properly selected.

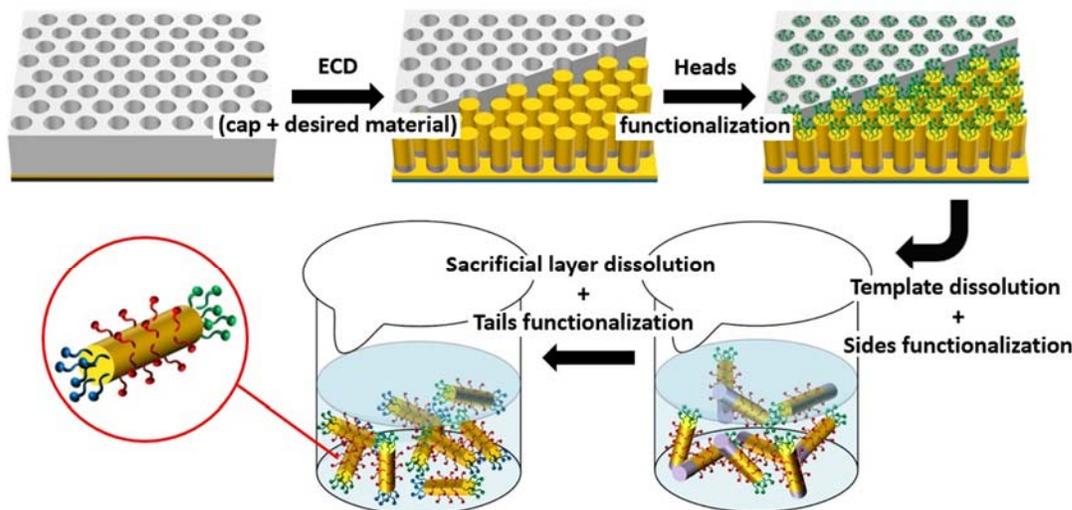


Figure 1: Strategy to manufacture spatially-decorated nanowires.

COLL 124

Correlating the interaction of colloidal nanoparticles with biological matter with their physicochemical properties

Wolfgang Parak, *wolfgang.parak@uni-hamburg.de. Universitaet Hamburg, Hamburg, Germany*

Colloidal nanoparticles (NPs) may be valuable tools for in vivo diagnosis and therapy in the future. Before they can be safely using in clinics, their interaction with the human body needs to be understood for each individual particles. This involves for example biodistribution (concerning targeting) as well as toxicity (concerning safety). In order to avoid testing of each new NP formulation from scratch, ideally the biological response of any new NP could be predicted by the physicochemical properties of the NP. While there are many studies about the impact of certain physicochemical NP properties on the biological response of NPs, as for example size-, shape-, surface coating-dependence, a reliable prediction based on the physicochemical properties is not possible. In this presentation some ideas towards making better predictions will be presented.

COLL 125

Structure-function relationships in the development of immunotherapeutic agents

Chad A. Mirkin, *chadnano@northwestern.edu. Chemistry, Northwestern University, Wilmette, Illinois, United States*

To achieve a robust and powerful response with immunotherapeutic agents, both an adjuvant, to activate the innate immune system, and an antigen, to direct the immune response, must be delivered. Currently, it is not clear if both components need to be delivered to the same cell, and if temporal control of the two signals is required for maximum activation. Since it is difficult to modulate spatiotemporal delivery with most delivery systems, these questions have not been thoroughly investigated. However, the spherical nucleic acid (SNA) platform, which consists of a dense shell of oligonucleotides conjugated to a nanoparticle core, is ideal for this task due to its extremely modular architecture and unique properties (e.g., rapid cellular uptake and increased resistance to nuclease degradation) compared to linear nucleic acids. SNAs composed of immunomodulatory oligonucleotides and tumor-specific antigens induce the immune system to clear tumors, and are thus promising as cancer vaccines. Since the mechanism through which the antigen and adjuvant are assembled into the SNA is easily modified, this can be used to control when and where the adjuvant and the antigen signals are delivered. Here, we incorporate both the adjuvant and antigen on the SNA via different encapsulation and conjugation schemes to study the spatiotemporal control of the two signals and its effect on tumor clearance. Hybridizing a peptide-oligonucleotide conjugate to the oligonucleotide shell of the SNA increased the speed of peptide presentation compared to either encapsulating the antigen or

conjugating it to the surface of the nanoparticle with a lipid anchor. We found that this change in kinetics resulted in increased activation of the T cells *in vivo*, which in turn caused increased tumor cell clearance. Furthermore, we generalized this approach for the attachment of any peptide antigen by using universal linkers that utilize to the N-terminus. Since small changes to the peptide structure cause dramatic changes in the antigenicity of the peptide, we reasoned that traceless and reversible linkers would increase T cell activation. Indeed, we found that antigen-specific T cell activation could be increased an order of magnitude when peptide linkers with readily reversible and traceless chemistries (i.e., disulfide bonds) as opposed irreversible chemistries (i.e., thiol-maleimide conjugation) were used.

COLL 126

Designer nanoparticles for intracellular targeting and delivery

Teri W. Odom, todom@northwestern.edu. Northwestern University, Evanston, Illinois, United States

Gold nanoparticles (AuNPs) are promising as delivery agents, but the influence of key design parameters such as size and shape of the particle core and ligand density is incomplete. This talk will describe a side-by-side comparison of three different AuNP cores (13-nm spheres, 50-nm spheres, and 40-nm stars) with the same oligonucleotide surface density applied to two different systems. First, we will discuss how different NP cores affect the intracellular distribution and delivery of siRNA. Second, we will examine how different NP cores with CpG ligands affect immunostimulatory activity. Finally, we will describe the promise and challenges of designing a nanoparticle platform for delivering specific ligands in different cellular systems.

COLL 127

Improving antitumor immunity through immuno-engineering

Michael Goldberg, michael_goldberg1@dfci.harvard.edu. Dana-Farber Cancer Institute, Boston, Massachusetts, United States

Cancer immunotherapy can confer durable benefit to patients, but the proportion of responders remains low. We have developed drug delivery systems that can focus the action of immunotherapy on the cells of interest. Altering the biodistribution, co-localization, and pharmacokinetics of immunomodulatory compounds can improve efficacy and safety.

COLL 128

Interactions of amphiphilic ligand-coated gold nanoparticles with cells and tissues from the nano- to macro-scale

Darrell J. Irvine, *djirvine@mit.edu*. *Massachusetts Inst of Tech, Cambridge, Massachusetts, United States*

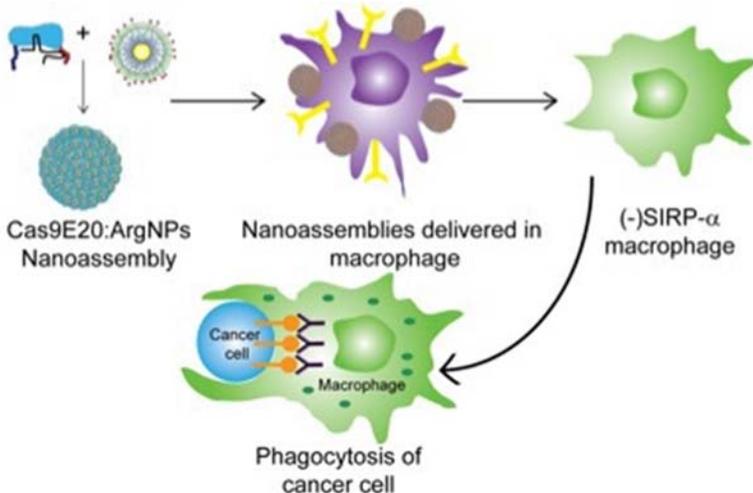
We synthesized gold nanoparticles soluble in physiologic solutions via an amphiphilic sulfonate-terminated alkanethiol organic ligand shell. The capacity of the organic ligand shell to accommodate guest molecules and reorganize in response to the local environment endows these particles with a variety of properties of interest for biomedical applications. In vitro, these particles can embed within and penetrate through lipid bilayers without permanent membrane disruption in both model membranes and live cells. Across a narrow range of particle diameters and ligand compositions, these particles exhibit other striking interactions with lipid bilayers, exhibiting membrane fusogenic properties and intra-membrane aggregation behavior. In addition, the organic ligand shell can efficiently sequester hydrophobic drugs for delivery into cells. When targeted to specific cells via conjugation to antibodies, their cell-penetrating behavior can be arrested until the conjugate is internalized into endosomes, where the targeting ligand is degraded. In vivo, we find that the biodistribution of these particles is significantly influenced by the composition of the organic ligand shell, and we demonstrate a dendritic cell-tropic particle composition that can be used to dramatically enhance the potency of peptide vaccines. Together these diverse properties suggest a variety of potential uses for ligand-coated gold nanoparticles in nanomedicine.

COLL 129

CRISPRed macrophages for cell-based cancer immunotherapy

Yi-Wei Lee¹, *yiweilee@umass.edu*, *Moumita Ray*², *Joseph Hardie*³, *Michelle E. Farkas*², *Vincent M. Rotello*². (1) *Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States* (2) *Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States* (3) *University of Massachusetts Amherst, Amherst, Massachusetts, United States*

The immune system plays a critical role in preventing tumor initiation and growth; evasion of this system is required for cancer progression. One such mechanism is the generation of “don’t eat me” signals by the interaction between CD47 on cancer cells and SIRP- α on macrophages to prevent phagocytosis. Here, we show an integration of nanotechnology/biology strategies for cancer immunotherapy that uses arginine nanoparticles (ArgNPs) to deliver CRISPR-Cas9 gene editing machinery into cells to generate SIRP- α knockout macrophages. The nanocomposite efficiently co-delivers single guide RNA (sgRNA) and Cas9 protein required for editing to knock out the “don’t eat me signal” in macrophages that prevents phagocytosis of cancer cells. Turning off this signal increased the innate phagocytic capabilities of the macrophages by 4-fold. This improved attack and elimination of cancer cells makes this strategy promising for the creation of ‘weaponized’ macrophages for cancer immunotherapy.



COLL 130

Multivalent bi-specific nanobioconjugate engager for targeted cancer immunotherapy

Christina von Roemeling^{4,2}, vonroemeling.christina@mayo.edu, Hengfeng Yuan^{9,4}, Wen Jiang³, Yaqing Qie⁴, Xiujie Liu⁵, Yuanxin Chen⁴, Yifan Wang³, Robert Wharen¹, Kyuson Yun⁶, Guojun Bu⁴, Keith Knutson⁷, Betty Y.S. Kim⁸. (1) Neurosurgery, Mayo Clinic, Jacksonville, Florida, United States (2) Mayo Clinic School of Biomedical Science, Rochester, Minnesota, United States (3) Radiation Oncology, The University of Texas MD Anderson Cancer Center, Houston, Texas, United States (4) Neuroscience, Mayo Clinic, Jacksonville, Florida, United States (6) Neurosurgery, Houston Methodist, Houston, Texas, United States (7) Immunology, Mayo Clinic, Jacksonville, Florida, United States (8) Neurosurgery, Cancer Biology, Neuroscience, Mayo Clinic, Jacksonville, Florida, United States (9) Orthopedics, Fudan University, Shanghai, China

Although advances in immunotherapy research have ushered in a new era of cancer treatment that tout the possibility of achieving curative outcomes in patients even with metastatic disease, strategies such as immune checkpoint blockade only demonstrate efficacious outcomes in select 'immunogenic' cancers. Immunogenicity in cancer is largely defined by antigenicity where higher mutational burden correlates with immune infiltration in the tumor, serving as a biomarker for response. For the vast majority of cancer, antigenicity falls short of the predictive margin, and these immunologically 'cold' tumors effectively circumvent immune surveillance mechanisms. Using colloidal nanoparticles as substrates, we create a multivalent bi-specific nanobioconjugate engager (mBiNE) that bridges the interaction between cancer cells and macrophages. Using simple conjugation chemistry, mBiNE exhibits a tumor receptor targeting antibody as well as an immune activating moiety- a method that is highly versatile and can be tailored to accustom unique cancer microenvironments. In this study we target mBiNE to human epidermal growth factor receptor 2 (HER2) on breast cancer cells, and simultaneously stimulate their phagocytic uptake with calreticulin (CRT) which interacts

with lipoprotein receptor-related protein 1 (LRP1) on macrophages. We show that mBiNE directs recognition and clearance of cancer cells, and is capable of initiating adaptive immune responses that result in tumor clearance and durable anti-tumor immunity in syngeneic preclinical models.

COLL 131

Engaging nanoparticle-cell interactions through “smart” design

Marilyn R. Mackiewicz, *mackiewi@pdx.edu*. Chemistry, Portland State University, Beaverton, Oregon, United States

A central theme in nanotechnology designed for biomedical applications is the intelligent design of “smart” nanomaterials for translational applications such as drug delivery, sensing, cell-labeling, and imaging. These engineered nanomaterials must be designed to interact with and function in a living host environment without undergoing biological transformations that result in loss of function and stability. To achieve such systems, we must fill the gap in knowledge regarding our understanding of how the architectural design of nanomaterials affects nanoparticle-biological interactions (NBIs) such as their biological transformations, motility, endocytosis, exocytosis, and clearance mechanisms. Furthermore, given the critical need to successfully transform nanomaterials into efficient drug delivery and imaging agents, well-defined nanomaterials with tightly-controlled size and shape whose NBIs are well understood are of significant interest. Here we will describe the design of membrane encapsulated nanoparticles of varying size, shape, and surface composition. A variety of surface architectures designed to engage and enhance cellular uptake will be presented and discussed. We will also examine how the structure of the surface ligands and their charge affect cellular uptake, retention, and toxicity *in vitro* using a variety of cell lines and *in vivo*. Transmission electron and confocal microscopy will be used to visualize the uptake of the nanomaterials. Collectively, we expect that the use of well-characterized AuNPs of constrained shape, size, and surface architecture should allow us to tease apart specific nanoparticle features that drive NBIs and mechanisms of endocytosis and exocytosis so that we can harness this knowledge to redirect their behavior to overcome their translational barriers *in vivo*.

COLL 132

Nanoparticulate delivery systems for RNA therapy and genome editing

Daniel G. Anderson, *dgander@mit.edu*. Chemical Engineering, Institute for Medical Engineering and Science, Harvard-MIT Division of Health Sciences & Technology, David H. Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

High throughput, combinatorial approaches have revolutionized small molecule drug discovery. Here we describe our work on the combinatorial development of nano

particulate delivery systems for RNA delivery and gene editing systems. Libraries of degradable polymers and lipid-like materials have been synthesized, formulated into nanoparticles, and screened for their ability to deliver RNA, both in vitro and in vivo. A number of delivery nanoformulations have been developed with in vivo efficacy, and show potential therapeutic application for the treatment of genetic disease, viral infection, and cancer.

COLL 133

Discovery and translation of the cell membrane-coated nanoparticle technology

Liangfang Zhang, zhang@ucsd.edu. Nanoengineering, MC-0448, University of California San Diego, La Jolla, California, United States

The emerging nanotechnology in biomedicine has sparked new hope for the treatment and diagnosis of various important human diseases. However, development of functional nanomaterials and nanodevices can be encumbered by unanticipated material properties and biological events, which can negatively impact their effectiveness when introduced into complex, physiologically relevant systems. In this talk I will report on the preparation of a polymeric nanoparticle enclosed in the plasma membrane of natural human cells (e.g., RBCs, platelets, cancer cells, etc). The resulting cell membrane-coated nanoparticles are demonstrated to possess many surface functions of natural cells via studies of interactions with plasma proteins, cells, tissues, and microorganisms. Such multifaceted cell-mimicking properties can be attributed to the preservation of biomembrane on nanoparticle surfaces, which facilitates the display of intricate biochemistry that is difficult to replicate using conventional functionalization approaches. As the platform is entirely biocompatible and biodegradable, it can be applied toward a myriad of biomedical applications, including drug delivery, detoxification and vaccination, where the vast implications of cell surface properties may benefit a variety of disease treatments.

COLL 134

Modified macrophages as cell-based delivery tools and therapeutic entities for cancer

Michelle E. Farkas, farkas@chem.umass.edu. Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States

The processes of tumor invasion and establishment of distant metastases are the boundaries beyond which manageable cancers become untreatable; tumor associated macrophages (TAMs) are critical to enable and sustain these growths. TAMs have been correlated with tumor angiogenesis, invasion and metastasis, and poor patient prognoses. They have also been shown to home to and silence the immune response to tumors. In our work, we are taking advantage of their innate characteristics and manipulating macrophages for: (1) their use as imaging and delivery agents, and (2)

therapeutic entities in and of themselves. Toward the first aim, we present effects of surface functionalization of macrophages via various chemical methods, demonstrating that the cells retain viability, along with their homing and phagocytic characteristics. These cells also continue to migrate to and interact with cancer models, *in vitro* and *in vivo*. In the second objective, we have converted macrophages into enhanced tumor-fighting entities by employing an arginine-nanoparticle CRISPR-Cas9 delivery system in order to knock out SIRP-a, or the “don’t eat me” signal. The edited cells possessed enhanced abilities to phagocytose cancer cells. This cell based platform will lay the ground-work for the generation of new cell based entities that can be used to image and treat cancers, with enhanced specificity and tumor penetration.

COLL 135

Overcoming biological barriers for circulation and targeting of nanoparticles

Samir Mitragotri, mitragotri@seas.harvard.edu. School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States

Nanoparticle-based drug delivery systems aim to improve the biological outcome of encapsulated drugs for therapeutic effects. However, nearly all synthetic materials, polymeric particles included, suffer from certain limitations *in vivo*. Poor vascular circulation, limited targeting and the inability to negotiate many biological barriers have prevented the overwhelming majority of polymeric particle drug delivery systems from entering the clinic. To further complicate the matter, the above requisites must be performed simultaneously while also limiting toxic effects to the patient. While attempts are being made to design such multifunctional carriers, the use of circulatory cells to augment the function of synthetic nanoparticles offers an exciting opportunity. I will discuss systems that make simultaneous use of natural systems (circulatory) cells and polymeric systems (synthetic nanoparticles) to improve circulation and targeting. Specific examples of such hybrid systems include adsorption of nanoparticles to the surface of red blood cells for prolonged circulation and lung targeting *in vivo*, and attachment of particles to the surface of monocytes for specific targeting to inflamed tissues *in vivo*. These hybrid systems offer a new design paradigm for nanomedicine.

COLL 136

Tolerogenic nanoparticles for the prevention of anti-drug antibodies - from concept to the clinic

Lloyd Johnston, ljohnston@selectabio.com. Selecta Biosciences, Watertown, Massachusetts, United States

The development of anti-drug antibodies (ADAs) is a common cause for treatment failure and adverse events associated with biologic therapies. Selecta Biosciences has recently demonstrated that synthetic vaccine particles encapsulating rapamycin (SVP-Rapamycin), but not free rapamycin, are capable of inducing durable antigen-specific

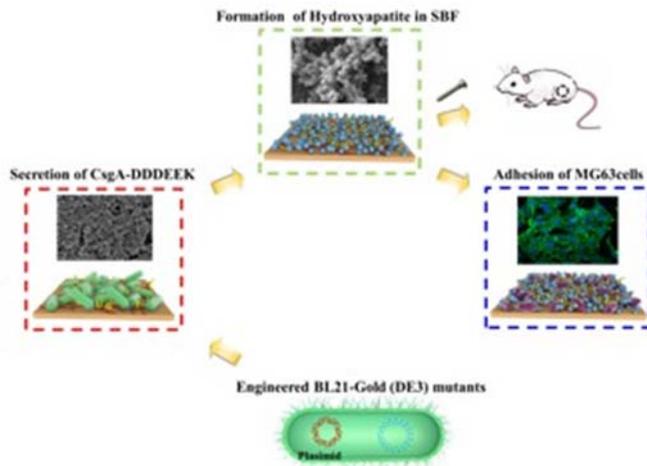
immune tolerance when co-administered with antigen in mice and nonhuman primates. The tolerogenic response is characterized by induction of tolerogenic dendritic cells and antigen-specific regulatory T cells. Here we provide examples of combining SVP-Rapamycin with three immunogenic biologics, coagulation factor VIII in a model of hemophilia A, an immunotoxin in a tumor model, and pegylated uricase in hyperuricemic mice as well as applications in gene therapy. In all examples, SVP-Rapamycin induced durable immune tolerance and improved therapeutic outcome in animal models of disease. Additionally, initial clinical data will be discussed from Selecta's Phase 1 and ongoing Phase 2 trial of SEL-212, a combination of the biologic pegsiticase (pegylated uricase) and SVP-Rapamycin for the treatment of chronic severe gout. Adjunct therapy with SVP-Rapamycin represents a novel and potentially broadly applicable approach to prevent ADAs against biologics and improving the safety and efficacy profile across a wide range of biologic therapies.

COLL 137

Universal and ultrastable mineralization coating bioinspired from biofilms

Yang Xiao^{1,2}, 317190026@qq.com. (1) Sichuan University, CHENGDU, Sichuan, China
(2) Wyss Institute at Harvard, Boston, Massachusetts, United States

A simple and universal method for manufacturing a mineralization coating on various surfaces was developed using a biofilm-based material obtained from engineered curly nanofibers. The amyloid protein (CsgA), is the main proteinaceous component in the *Escherichia coli* (*E. coli*) biofilm, which can withstand detergents in harsh environment. The peptide sequence DDDEEK is bioinspired from salivary acquired pellicles in the dental plaque biofilm, having a strong ability to absorb mineral ions and induce the formation of biominerals. The bioinspired coating was successfully secreted by the engineered *E. coli* which was transformed with recombinant PET-22b-CsgA-DDDEEK plasmid. The coating could be manufactured on virtually any type of material surface. Moreover, the new coating could bear shear force and stay on diverse slices for at least one month. Furthermore, compared with bare slices, the coated slices had a better mineralization performance in terms of the morphology of the newly generated crystals and their mechanical properties. The bioactive hydroxyapatite (HA) layer induced by the coating could improve the adhesion, proliferation, and osteodifferentiation of MG63 cells. In animal experiment, the coated Ti₆Al₄V screw with induced HA could efficiently improve its biocompatibility, osteogenicity and osseointegration, thus the coating is highly promising for biomedical applications.



COLL 138

Adaptive treatment tolerance attenuated by nanotechnology-assisted drug delivery

Xing-Jie Liang, xingjieliang@hotmail.com. University of Chinese Academy of Sciences, Beijing, China

Adaptive treatment tolerance (ATT) is one of the main obstacles in the therapeutic failure of metastasis cancer treatments in clinic. Several factors in treatment tolerance include MDR-associated proteins overexpressed in cells, inactivation of therapeutic molecules in targeted tissues, invalidation of treatments in patients, etc. This clinical obstacle was broadly explored, and different molecular mechanisms were clarified with enhanced repair mechanisms of drug induced DNA damage, lowered tumor extracellular pH, alteration of cell cycle check points, blockage of apoptosis pathway and poor tumor vasculature, respectively. There is still no significantly clinical improvement so far. Nanotechnology has been widely used in the development of new strategies for drug delivery and cancer therapy. Compared to traditional drug delivery systems, nanoscale drug delivery systems (NDDS) have greater potential in many areas, such as multiple targeting functionalization, combined drugs delivery, longer circulation time and systemic control release. NDDS incorporating stimulus-responsive biopolymer have remarkable properties which allow them to bypass biological barriers and achieve targeted intracellular drug delivery. Some of these have been translated from the bench to clinical application and approved by the Food and Drug Administration (FDA) for treatment of various cancerous diseases. With further development of biocompatible nanoformulations, it might be possible to design even more promising multiple-responsive NDDS synergistic for combined drug delivery and efficient cancer therapy in the future. Nanotechnology-based drug delivery is expected to bring new hope for cancer treatment by enhancing anticancer drug efficacy, overcoming drug resistance and reducing drug toxicity. This presentation describes the characteristic features of tumor resistance to classical chemotherapy and their mechanisms with the aid of nanoparticles for the development of newer drug delivery systems to overcome ATT in vitro and vivo.

COLL 139

Leverage physiology for bioresponsive drug delivery

Zhen Gu, *guzhenlab@gmail.com*. Joint Department of Biomedical Engineering, University of North Carolina at Chapel Hill and North Carolina State University, Chapel Hill, North Carolina, United States

Spurred by recent advances in materials chemistry, molecular pharmaceuticals and nanobiotechnology, stimuli-responsive "smart" systems offer opportunities for precisely delivering drugs in dose-, spatial- and temporal-controlled manners. In this talk, I will discuss our ongoing efforts in developing physiological signal-triggered bio-responsive drug delivery systems, especially based on artificial cells or engineered cells. I will first present the glucose-responsive synthetic systems for biomimetic delivery of insulin for diabetes treatment. Bio-responsive microneedle patches and vesicle fusion-mediated synthetic beta cells will be emphasized. I will further discuss the local and targeted delivery of immunomodulatory therapeutics for enhanced cancer therapy. Our latest study utilizing platelets and injectable hydrogels for targeted/local delivery of immune checkpoint inhibitors will be specifically introduced.

COLL 140

Insulin – containing silica nanoparticles with a high loading capacity and demonstration of bioactivity: Potential for oral delivery

Delyan Hristov¹, *hristovdr@gmail.com*, **Fiona McCartney**¹, **Jason Beirne**¹, **Stephanie Reid**², **Eugene A. Mahon**², **Sourav Bhattacharjee**¹, **Gareth Redmond**², **Dermot Brougham**², **David J. Brayden**¹. (1) School of Veterinary Medicine, University College Dublin, Dublin, Ireland (2) School of Chemistry, University College Dublin, Dublin, Ireland

Nanoparticle technologies for drug delivery have attracted interest due to their beneficial physicochemical properties that can create opportunities to improve pharmacokinetics and toxicology profiles of existing molecules, for example by solubilising hydrophobic molecules and decreasing clearance. Macromolecules including peptides and proteins currently dominate development pipelines, however they are currently limited to injectable formats. Two problems prevent their oral delivery: (i) instability due to enzymatic degradation and (ii) low small intestinal epithelial permeability. Approaches to enable oral peptide delivery typically involve permeation – enhancers and/or nanotechnology. Here, we created a silica – based nanoparticle construct with loading capacity of human insulin which may be suitable for oral administration. The physicochemical properties of the nanoparticles were studied using dynamic light scattering, transmission electron microscopy, and zeta potential, HPLC and ¹H nuclear magnetic resonance were used to determine peptide association efficiency and protein content. The hydrodynamic diameter range was found to be 100 – 400 nm, with a relatively high loading capacity (≥ 40%), as measured by HPLC. The reproducibility of

the synthesis was evident from a batch – to – batch variability in size and loading of ~10%. The retention of secondary structure of particle – released insulin was confirmed by circular dichroism (CD), while bioactivity was demonstrated in rats following sub – cutaneous administration of a 1 IU/kg dose. Finally, the particle released insulin increasingly more rapidly as the pH and salinity of the media was increased. Importantly dissolution occurred in the span of a several hours at pH 2.3, as is necessary for stability in the stomach. We are currently evaluating the silica – based particles potential for oral delivery in a rat model.

COLL 141

Helical polymer structure provides platinum-loaded polymeric micelles with favorable size and stability for effective tumor-targeting

Yuki Mochida¹, *mochida-y@kawasaki-net.ne.jp*, **Horacio Cabral**², **Yutaka Miura**², **Kensuke Osada**², **Nobuhiro Nishiyama**³, **Kazunori Kataoka**^{1,4}. (1) Innovation Center of NanoMedicine, Kawasaki Institute of Industrial Promotion, Kawasaki, Kanagawa, Japan (2) Department of Bioengineering, The University of Tokyo, Tokyo, Japan (3) Laboratory for Chemistry and Life Science, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan (4) Policy Alternatives Research Institute, The University of Tokyo, Tokyo, Japan

Polymeric micelles are promising nanoscale delivery carriers for a wide range of therapeutic agents. Complexation of hydrophobic anticancer drug (1,2-diaminocyclohexane)platinum(II) (DACHPt) with poly(ethylene glycol)-poly(glutamic acid) block copolymers gives DACHPt-loaded polymeric micelles (DACHPt/m), which exerted high antitumor efficacy against xenograft models of various solid tumors due to its efficient tumor accumulation and are currently investigated under clinical trials. In this study, we demonstrated that α -helix was formed in the DACHPt-conjugated P(Glu) chains, which consists of the core of DACHPt/m, and significantly controlled their size distribution and drug delivery performance. DACHPt/m prepared from PEG-P(Glu) with an ability to form α -helix, *i.e.* PEG-poly(L-glutamic acid) and PEG-poly(D-glutamic acid), had an average size of 30 nm with low polydispersity, whereas DACHPt/m prepared from PEG-P(Glu) without an ability to adopt regular secondary structures, *i.e.* PEG-poly(D,L-glutamic acid), showed an average size of 55 nm with relatively high polydispersity. Circular dichroism spectrometry demonstrated that 50% region of the P(Glu) segment in L- and D-DACHPt/m formed α -helix. Considering drug loading of the micelles was independent of the stereoregularity of P(Glu) segment, the size distribution of DACHPt/m could be controlled by α -helix formation. In physiological condition, chloride ions induced DACHPt release from the micelles, leading to micelle dissociation. Interestingly, the DACHPt/m with α -helix showed slow drug release and micelle dissociation at constant rate by keeping their original size, whereas the DACHPt/m without regular secondary structures disintegrated in an accelerated manner while increasing their size. This sustained disintegration process of the DACHPt/m with α -helix was advantageous for avoiding uptake by the liver and spleen and prolonging blood circulation, which eventually augmented tumor accumulation and enhanced antitumor efficacy against pancreatic tumor xenograft models. Introducing secondary

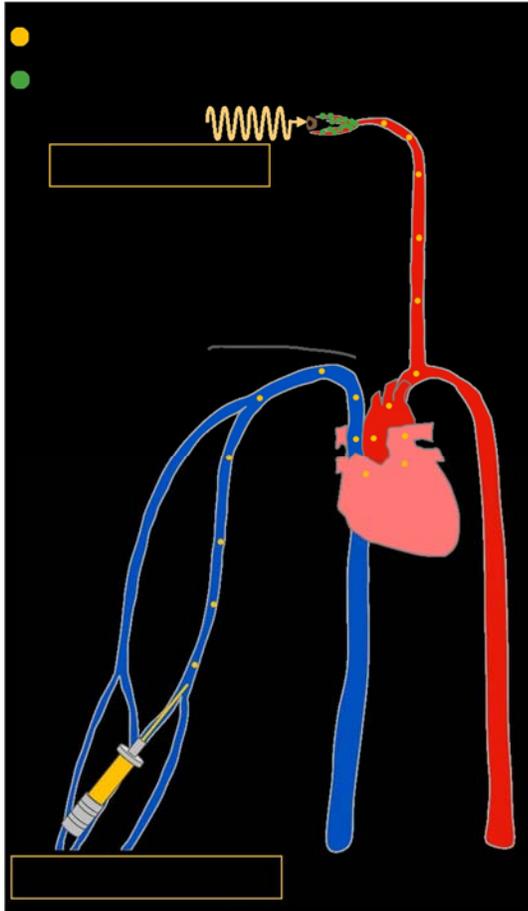
structures in the core of polymeric micelles could be a feasible strategy to control their size and stability for desirable tumor targeting performance.

COLL 142

Photo-targeted nanoparticles for intravenous treatment of choroidal neovascularization

Yanfei Wang¹, *yanfeiw.2013@gmail.com*, Daniel S. Kohane². (1) Harvard Medical School, Boston, Massachusetts, United States (2) Anaesthesia, Boston Children's Hospital, Harvard Medical School, Newton, Massachusetts, United States

Choroidal neovascularization (CNV) is the major cause of vision loss in wet age-related macular degeneration (AMD). Current therapies require repeated intravitreal injections, which are painful and can cause infection, bleeding, and retinal detachment. We developed a drug delivery system that can be administered intravenously and accumulate in the back of the eye by light-triggered targeting. Photo-targeted nanoparticles (NP-[CPP]) were formed from PEG-PLA chains modified with cell penetrating peptide (CPP). Cell uptake of NP-[CPP] was inactivated by attaching a photocleavable group DEACM to the CPP, which also placed [CPP] in the core of the nanoparticle, preventing it from interacting with cells. Irradiation with 400 nm (blue) light cleaved DEACM, releasing CPP from the NP core and rendering it active. This system was evaluated in mice with laser-induced CNV. After intravenous injection of NP-[CPP], irradiation at the eye cleaved DEACM, allowing NP accumulation in the choroidal neovascular lesions. NP-[CPP] with irradiation showed greater accumulation in neovascular lesions compared to the same nanoparticles without irradiation or nanoparticles without CPP. In the same mouse CNV model, NP-[CPP] loaded with doxorubicin significantly reduced neovascular lesion size. This phototriggered targeting strategy could allow non-invasive treatment of CNV and similar diseases, and enhance the proportion of drug in diseased areas of the eye vs. other healthy parts of the eye or body.



COLL 143

Oxidation-responsive nanolayered coatings for the on-demand delivery of therapeutic growth factors

John R. Martin^{1,2}, jrmart@mit.edu, **MayLin T. Funkenbusch**^{1,2}, **Sheryl Wang**^{3,2}, **Paula T. Hammond**^{1,2}. (1) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Koch Institute for Integrative Cancer Research at MIT, Cambridge, Massachusetts, United States (3) Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Many different polymeric scaffold materials that exhibit degradability and minimal toxicity have been developed as bone void fillers to promote tissue regeneration in large bone defects, but in general these materials do not intrinsically promote new bone growth. To this end, implants coated with electrostatic layer-by-layer (LbL) assemblies (Figure 1A) of polyelectrolyte polymers and pro-healing growth factor proteins such as bone morphogenic protein-2 (BMP-2) have been developed. However, current polyelectrolyte-based constructs are engineered to degrade by non-specific hydrolysis to mediate protein release and are minimally-responsive to the rate of tissue repair. This limitation motivates the need for LbL systems that better deliver therapies over the entire lifetime of the bone healing process. Therefore, we have developed stimuli-

responsive LbL nanofilms that selectively release drug payloads in response to cell-generated reactive oxygen species (ROS), yielding a system that prolongs the drug efficacy window by conserving therapeutics only until they are needed. Poly(thiokeetal- β -amino amide) (PTK-BAA) cationic polymers were synthesized by step-growth polymerization (Figure 1B); the polymer's thiokeetal and amide bonds are hydrolytically inert while thioketals are selectively degraded by ROS. When incorporated into LbL films with anionic poly(acrylic acid) and either the model cationic protein lysozyme (Figure 1C) or therapeutic protein BMP-2 (Figure 1D), these coatings experienced minimal protein release when incubated in PBS at 37°C but discharged significantly greater protein amounts when treated with physiological doses of hydrogen peroxide (H_2O_2). These data highlight the utility of PTK-BAA polymers as environmentally-responsive LbL film constituents and emphasize the potential of “on-demand” drug delivery systems in bone regenerative applications.

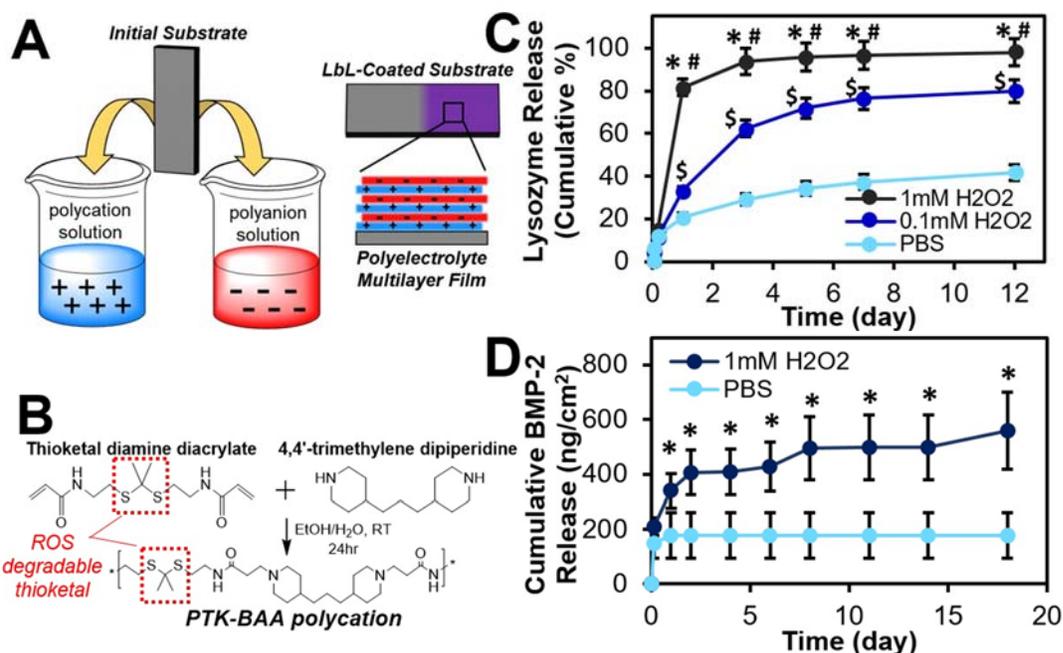


Figure 1. Layer-by-layer (LbL) assembly of polyelectrolytes created (A) multilayer films with (B) ROS-degradable PTK-BAA polycations, yielding coatings that selectively released encapsulated (C) lysozyme and (D) BMP-2 proteins after treatment with H_2O_2 .

COLL 144

Increasing nanoparticle drug loading efficiency via self-assembly

Mark W. Grinstaff, mgrin@bu.edu. Boston Univ Dept of Chem, Boston, Massachusetts, United States

The incorporation of chemotherapeutic agents into nanocarriers enhances the safety and efficacy of many anticancer agents. However, maximization of drug to material

efficiency (i.e., drug loading) is challenging, as most drugs are encapsulated at 5-15 wt% loadings. To overcome this shortcoming, a novel self-assembly approach is utilized to fabricate a dual-loaded poly(1,2-glycerol carbonate)-*graft*-succinic acid-paclitaxel (PGC-PTX) conjugate nanoparticle (NP) in which the physical entrapment of free paclitaxel (PTX) affords unprecedented ultra-high drug loadings > 100 wt% and tunable release kinetics. Despite high incorporation of free PTX (up to 50 wt%), the dual-loaded PGC-PTX nanocarriers (i.e., PGC-PTX + PTX NPs) exhibit controlled and sustained drug release over 15 days, without burst release effects. Importantly, optimization of drug/material efficiency concomitantly affords improved *in vitro* efficacy. *In vivo*, PGC-PTX + PTX NPs are safely administered at doses exceeding the median lethal dose of standard PTX, while a single high dose significantly extends survival relative to weekly PTX administrations in a murine model of peritoneal carcinomatosis.

COLL 145

Block copolymer nanocarriers with peptide units for drug delivery

Markus Klapper, klapper@mpip-mainz.mpg.de, Filiz Karagoez, Nicole Wutke. Max-Planck-Institute for Polymer Research, Mainz, Germany

Block copolymers are outstanding materials owing in large to their self-assembly behavior in solution which makes them ideal candidates for drug delivery applications. Both aqueous and nonaqueous emulsion techniques can be applied for the formation of biocompatible polylactide-based nanocarriers. By using pseudo poly(amino acid)s, a new type of hydrolysable polylactide block copolymer was synthesized and their aggregation behavior was investigated. Remarkably, these polymers can be functionalized in different ways due to their pending amino groups in the side chain. Also thiol functionalized polymers will be shown. Moreover, specific peptide sequences were incorporated into PLLA blocks via nonaqueous emulsion to allow for selective drug release at cancer cells. The polylactide-block-peptide-block-polylactide triblock copolymer was synthesized by initiation of the ring-opening polymerization of L-lactide with a complex bifunctional peptide. The peptide sequence provides an enzymatic recognition and cleavage site for bisection by MMP-2 which is overexpressed in tumor tissue

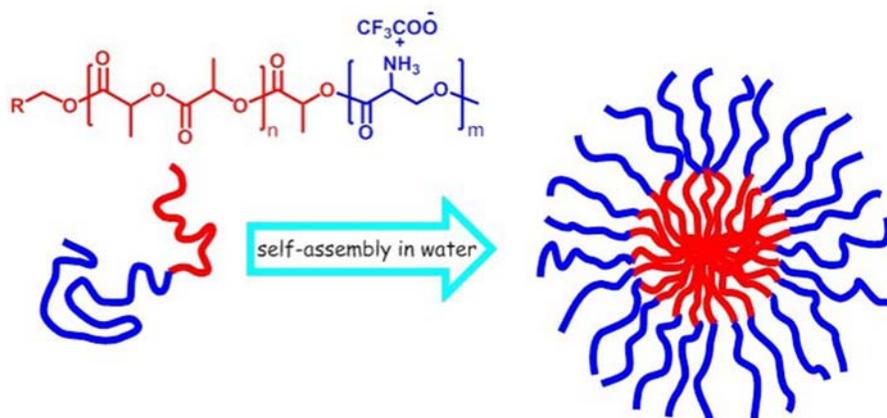


Figure 1: Self-assembly of Poly(L-lactide)-*b*-poly(L-serine ester) copolymer

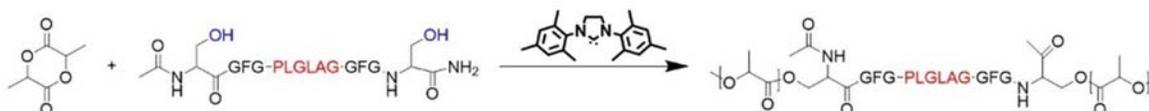


Figure 2: Ring opening polymerization of L-lactide by functional peptides

COLL 146

NIH/NIBIB funding for novel drug delivery technologies

David Rampulla, david.rampulla@nih.gov. National Institute of Biomedical Imaging and Bioengineering, Bethesda, Maryland, United States

The NIH has long supported the development of novel drug delivery technologies, both tailored for the treatment of specific diseases and as platform technologies. This presentation will highlight trends in funding for drug delivery research at NIH over the last few years, with a focus on the portfolio at the National Institute for Biomedical Imaging and Bioengineering (NIBIB). The talk will also highlight specific funding opportunities of interest and discuss some strategies for navigating the NIH application process.

COLL 147

Single-atom alloy catalysts: From theory to working catalysts through surface science characterization

Theodore Thuenig², thuenig@uwm.edu, Matt Darby¹, Romain Reocreux¹, Angelos Michaelides¹, Michail Stamatakis¹, E Charles H. Sykes². (1) UCL, London, United Kingdom (2) Tufts University, Medford, Massachusetts, United States

Recently, single-atom alloy catalysts composed of highly active metals dispersed in a more inert host have shown to be viable catalysts for industrially relevant reactions. These studies have benefitted from extensive surface science analysis and microscopy through the identification of active sites, intermediates, and reaction pathways. Integral to the success of both surface science studies and working catalysts is a comprehensive, predictive screening by density functional theory. Using theory as a roadmap, new single atom-alloy combinations are being developed by the Sykes group for hydrogenation, dehydrogenation, and carbon-carbon coupling reactions. Here we report characterization and catalytic advances in Ni and Pd single-atom alloy systems utilizing Au(111) as an inert host. These studies were performed with an array of surface sensitive techniques including temperature programmed desorption, X-ray photoelectron spectroscopy, and scanning tunneling microscopy to elucidate the mechanisms for catalytically relevant hydrogenation, dehydrogenation and oxidation reactions.

COLL 148

Selective oxidation of ethanol to acetaldehyde over TiO₂/Au(111)

Ashleigh Baber, ashleigh.baber@gmail.com, David T. Boyle, Jeremy Wilke, Vivian H. Lam. James Madison University, Harrisonburg, Virginia, United States

Depending on the surface preparation conditions, Au(111) supported TiO₂ nanoparticles react with small alcohols to form either reduced and oxidized products. The desire to selectively form oxidized or reduced products merits an investigation of alcohol reactivity over differently prepared TiO₂/Au(111) surfaces. In this work, a systematic study of ethanol reactivity over several TiO₂/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO₂/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x ($x < 2$). Atomic force microscopy (AFM) provides information regarding the structure of the Au(111) supported TiO₂ nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) monitors the selectivity of the reaction between ethanol and TiO₂/Au(111). Low coverages of fully oxidized TiO₂ nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

COLL 149

Influence of structure and composition on the surface chemistry of bimetallic Cu/Au model catalysts

Christopher Baddeley, cjb14@st-andrews.ac.uk, Federico Grillo, Rory Megginson, Stephen Francis. Eastchem School of Chemistry, University of St Andrews, St Andrews, United Kingdom

Supported Au nanoparticles have been shown to be capable of highly selective hydrogenation catalysis. However, catalytic activity is limited by the weak ability of Au to

dissociate molecular hydrogen and leads to a requirement to use high pressures of hydrogen gas in such processes. A promising alternative approach, which operates efficiently at 1 bar pressure, utilizes the Cu-catalysed dehydrogenation of a secondary alcohol (2-butanol) to supply hydrogen for the desired hydrogenation process – in this case the selective conversion of furfural to furfuryl alcohol over Au. Optimization of this type of catalytic system is facilitated by a detailed understanding of the surface chemistry of each reagent over Au, Cu and Cu/Au surfaces including ordered surface alloys. A combination of complementary surface characterization techniques including scanning tunnelling microscopy, surface vibrational spectroscopy, X-ray photoelectron spectroscopy and temperature programmed desorption have been employed to investigate the influence of surface composition on the adsorption and thermal behavior of 2-butanol and furfural on Cu/Au surfaces.

COLL 150

Comparison of oxygen adsorption and absorption on rhodium, silver, and stepped platinum surfaces

Daniel R. Killelea¹, dkillelea@luc.edu, Rachael Farber¹, Marie Turano¹, Ludo Juurlink², Erin V. Iski³. (1) Loyola University Chicago, Chicago, Illinois, United States (2) Leiden University, Leiden, Netherlands (3) Chemistry and Biochemistry, University of Tulsa, Tulsa, Oklahoma, United States

The interaction of oxygen with the surfaces of catalytically active transition metals has attracted much interest because of the relevance to heterogeneous catalysis. Recently, we have shown that oxygen coverages in excess of 1 ML are achievable using gas-phase atomic oxygen (AO) to dose the metal surfaces. This talk will discuss some recent results comparing the uptake of AO and O₂ on Ag(111), Rh(111), and stepped Pt surfaces. On Pt surfaces, the geometry of the monoatomic steps determines whether or not low temperature dissociative chemisorption of O₂ will occur. In addition, on Pt(553), prolonged exposure to AO does not result in O coverages in excess of a monolayer, suggesting the defects are not effective at promoting the formation of subsurface oxygen. Conversely, on Rh(111), subsurface oxygen readily forms from exposure to AO. Finally, the uptake of oxygen on Ag(111) is discussed; unlike Pt(553) or Rh(111), where little surface reconstruction occurs, Ag(111) undergoes several phase transformations as the oxygen coverage is increased. These results using AO demonstrate that UHV-compatible dosing can prepare the same surfaces resulting high pressure O₂ exposures, allowing for quantitative and structural analysis of the oxidized surfaces.

COLL 151

Syntheses, plasmonic properties, and catalytic applications of Ag-Rh core-frame nanocubes and Rh nanoboxes with highly porous walls

Dong Qin, *dong.qin@mse.gatech.edu*, Yun Zhang. *Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States*

We report a simple and general method for the production of Ag-Rh bimetallic nanostructures with a unique integration of plasmonic and catalytic properties exemplified by these two metals, respectively. When a Rh(III) precursor is titrated into a polyol suspension of Ag nanocubes held at 110 °C in the presence of ascorbic acid and poly(vinylpyrrolidone), Rh atoms are generated and deposited on the nanocubes. When the amount of Rh(III) precursor is relatively low, the Rh atoms tend to nucleate from the edges of the Ag nanocubes and then follow an island growth mode because of the relatively low temperature involved and the high cohesive energy of Rh. The Rh islands can be maintained with an ultrafine size of only several nanometers, presenting an extremely large specific surface area for catalytic applications. As the amount of Rh(III) precursor is increased, the galvanic replacement reaction between the Rh(III) and Ag nanocubes will kick in, leading to the formation of increasingly concaved side faces and increase in surface coverage for the Rh islands. Meanwhile, the resultant Ag⁺ ions are reduced and deposited back onto the nanocubes, but among the Rh islands. By simply controlling the amount of Rh(III) precursor, we observe the transformation of Ag nanocubes into Ag-Rh core-frame and then Ag-Rh hollow nanocubes with a high porous surface. Upon selective removal of Ag by wet etching, the hollow nanocubes evolve into Ag-Rh and then Rh nanoboxes with highly porous walls. While the Ag-Rh core-frame nanocubes show a unique integration of the plasmonic and catalytic properties characteristic of Ag and Rh, respectively, the Rh nanoboxes show remarkable activity toward the catalytic degradation of environmental pollutants such as organic dyes.

COLL 152

Surface chemistry of gold islands deposited on TiO₂(110)

R. M. Dulanga S. Somaratne, *dulanga_somaratne@student.uml.edu*, James E. Whitten. *Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States*

The deposition of metals on semiconducting surfaces and the chemical and electronic properties at the interface are important for numerous applications that include catalysis, optoelectronics and surface-enhanced Raman spectroscopy. Gold islands are known to enhance the photocatalytic efficiency of titanium dioxide by impeding the recombination rate of separated electron-hole pairs. In the present work, the growth of gold in ultrahigh vacuum on clean TiO₂(110) has been studied using X-ray photoelectron spectroscopy (XPS), and the effects of the metal on the electronic structure of the surface have been measured with ultraviolet photoelectron and inverse photoelectron spectroscopies (UPS and IPES). The band gap and presence of gap states for various metal doses have been investigated. Charge transfer and band-bending effects have been quantified, along with work function changes of the surface as a function of deposited gold. The photocatalytic oxidative properties of the Au/TiO₂(110) surface have also been studied using both ultraviolet (UV) and visible light

irradiation for various adsorbates, with and without the presence of oxygen in the vacuum chamber. The experimental results have been accompanied by DFT calculations.

COLL 153

Hydration mediated interfacial transitions on mixed hydrophobic/hydrophilic nanodroplet interfaces

Filip Kovacik, Halil Okur, Sylvie Roke, sylvie.roke@epfl.ch. EPFL, Lausanne, Switzerland

Interfacial and nanoscale phase transitions are of fundamental importance for climate, industry and biological processes. On planar extended interfaces surface freezing occurs when an alkane/surfactant layer in contact with water reaches a temperature a few degrees above the bulk freezing point. This phenomenon entails the freezing of the surface alkyl chains, and is purely associated with the oil phase and not the water. Using second harmonic and sum frequency scattering techniques we investigate surface structural transitions on nanoscale hexadecane oil drops covered with a very dilute layer of alkyltrimethylammonium (C_xTA^+) ions in water. We find that on the nanoscale the behavior is significantly different from planar extended interfaces: Surface transitions are found that occur at temperatures a few degrees above the bulk super-cooled freezing point and not the bulk freezing point of the oil drops. The transitions involve all three interfacial constituents, the oil, the water and the surfactant, and are triggered by changes in the hydration structure of the alkyltrimethylammonium groups. Transitions do not occur for positively charged and not negatively charged. These results show remarkable difference related to the length scale of the system. Nanoscale droplets do not display the same interfacial structure and chemistry as extended planar interfaces of the same chemicals.

COLL 154

Molecular insight into the carboxylic acid – alkali metal cations interactions: Reversed affinity and ion pair formation

Adrien P. Sthoer¹, sthoer@kth.se, Jana Hladilková², Mikael Lund², Eric Tyrode¹. (1) Chemistry, KTH Royal Institut of Technology, Stockholm, Sweden (2) Theoretical Chemistry, Lund University, Lund, Sweden

Ion specific effect play an important role in a number of biological processes occurring in living organisms. However, a comprehensive molecular understanding remains elusive. It is currently believed that molecular interfacial interactions, including specific ion adsorption together with the concurrent disruption of the water structure in the direct proximity of functional groups, are the underlying key steps. Herein we present a vibrational sum frequency spectroscopy (VSFS) investigation of ion pair interaction between monovalent ions and the carboxylic acid moiety of a fatty acid Langmuir

monolayer at the liquid/vapour interface.

VSFS is a non-linear optical technique with an exquisite surface specificity that probes molecular orientation and allows determining the charging of the monolayer, including the formation of contact ion pairs with the carboxylate headgroups, giving a global insight into the study of the charged monolayer. The presentation focuses on two parts: a) Salt concentration and pH dependence of the interactions between the carboxylic acid and alkali metal chloride salts, where it is highlighted the specific ion interactions and a reversion of the cationic affinity with increasing pH. b) Molecular implications in terms of ion-pair formation during the 2D phase transition observed at high pH.

The addition of alkali metal chloride salts, LiCl, NaCl, and CsCl to the solution subphase causes the deprotonation of the monolayer. At a given ion concentration, the degree of deprotonation was found to be cation specific and strongly pH dependent. At low salt concentrations the surface charge values determined were found to be in agreement with Poisson-Boltzmann predictions. However, at high concentrations deviations were observed and more elaborate models that take into account steric effects were considered. Simulations yielded microscopic insight into the origin of pH dependence ion specificity, with the cations showing contrasting interaction preferences for either the uncharged carboxylic acid or the charged carboxylate. Although, below pH 9 the cation remain hydrated when interacting with the carboxylate, at higher pH the formation of contact ion pairs were observed.

The results provide exciting new insights into the complex interactions of alkali metal cations with the biophysically relevant carboxylic acid moiety.

COLL 155

Surface properties of hypobromite at the liquid-vapor interface studied by liquid jet XPS

Shuzhen Chen^{1,2}, *shuzhen.chen@psi.ch*, **Luca Artiglia**¹, **Fabrizio Orlando**¹, **Xiangrui Kong**^{1,3}, **Pablo Corral Arroyo**¹, **Markus Ammann**¹. (1) *Surface Chemistry Group, Paul Scherrer Institut, Villigen PSI, Villigen PSI, Switzerland* (2) *Environmental Science, ETH Zurich, Zurich, Switzerland* (3) *University of Gothenburg, Gethenburg, Sweden*

Solutions of hypobromite (OBr^-) have long been used as titrants, and OBr^- is a powerful oxidant. Oxidation of bromide (Br^-) to OBr^- is one of the important reactions to produce HOBr, which initiates the release of bromine out of the aqueous solution of sea water, sea spray or marine aerosols in the form of molecular halogen compounds that later drive O_3 depleting chemistry in the troposphere. The multiphase reaction of oxidation of Br^- to OBr^- involves an intermediate $[\text{BrOOO}]^-$, which has recently been shown to occur preferentially at the liquid-vapor interface and in that way provides for the route for efficient oxidation of bromide at the surface. It is crucial to get the surface properties of each species involved. The surface properties of Br^- have been investigated since a decade, with some open questions still. In turn, the surface propensities of OBr^- have

not yet been addressed at all.

OBr⁻ is unstable and disproportionates to bromide and bromate, and thus not many studies characterizing its properties in aqueous solution have been done. A common way to prepare OBr⁻ in aqueous solution is by adding bromine to a solution of an alkali metal hydroxide (e.g. adding Br₂ into NaOH aqueous solution in an ice-bath).

Here, we directly measure the surface propensity of OBr⁻ at the aqueous solution-air interface using the surface sensitive liquid jet X-ray photoelectron spectroscopy (XPS), performed at the Swiss Light Source (SLS), by aiming at depth profile information for OBr⁻ and Br⁻. We acquired Br 3d core level spectra of 0.08 M aqueous solutions composed of equal amounts of NaOBr and NaBr. The Br 3d region was fit by two spin-orbit split doublets, with the peak assigned to OBr⁻ separated by 2.2 eV from that of Br⁻. By varying the photoelectron kinetic energy and thus probe depth via variation of the probing photon energy, the Br 3d to O 1s signal intensity ratios increase with photoelectron kinetic energy for both, Br⁻ and OBr⁻. This indicates that both ions are rather depleted from the interface, in line with surface tension measurements for the case of bromide. This sheds light on mechanistic and structural aspects of the reaction of bromide with ozone. In the future, theoretical calculations as well as the first principle molecular dynamics simulations will be done to further explain the propensity of OBr⁻ at the liquid-vapor surface.

COLL 156

Using assembly of a chromonic mesogen to enable isolation and ligand-receptor binding studies of bacterial pilin protein

Arizza Ibanez, asibanez@syr.edu, Yan Y. Luk. Chemistry, Syracuse University, Syracuse, New York, United States

Fibrous assemblies of pilin protein on bacterial surfaces are responsible for a wide range biological functions of bacteria, including swarming motility, twitching motility, recognizing the sugar moieties (asialo- GM1) on mammalian cells, and the hydrophobic surface of abiotic surfaces, as well as playing an important role in horizontal gene transfer. To enable small molecule binding (ligand-receptor binding) studies to pilin for potential drug development, a method of isolating and purifying the whole pilin structure is needed. We discovered that 5'DSCG forms isodesmic assemblies in aqueous solution that sequesters water leading to non-denaturing aggregation or crystallization of proteins. We also found out that isodesmic assembly is promoted by peptides revealing a broad concentration range over which 5'DSCG forms detectable isodesmic assemblies prior to reaching liquid crystal formation concentration, lowering the "isodesmic-concentration" from 12 -14 wt% to ~1.5 wt%. We have developed a class of small organic molecules that bind and inhibit pili functions. Preliminary studies of ligand-pilin binding by using ¹⁵N heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance and circular dichroism (CD) show ligand binding induced structural changes.

COLL 157

Trapping of antibacterial agents within hydrophobic films of polyphosphazene polyelectrolytes

Victoria Albright¹, *victoria.albright.11@gmail.com*, **Hanna Hlushko**¹, **Haley Nelson**², **Cynthia Co**³, **Shabba Armbrister**^{4,5}, **Samantha Hernandez**⁴, **Matthew Andreo**³, **Arul Jayaraman**^{2,3}, **Alexander Marin**⁶, **Alexander K. Andrianov**⁶, **Svetlana A. Sukhishvili**¹. (1) *Materials Science and Engineering, Texas A&M University, College Station, Texas, United States* (2) *Chemical Engineering, Texas A&M University, College Station, Texas, United States* (3) *Biomedical Engineering, Texas A&M University, College Station, Texas, United States* (4) *College of Veterinary Medicine, Texas A&M University, College Station, Texas, United States* (5) *Entomology, Texas A&M University, College Station, Texas, United States* (6) *Institute for Bioscience and Biotechnology Research, University of Maryland, Rockville, Maryland, United States*

Direct layer-by-layer (LbL) assembly of cationic, small-molecule antibacterial bioactives with water-soluble, ionic polyphosphazenes (PPzs) containing trifluoroethoxy and carboxyl substituents is reported. First, influence of PPzs hydrophobicity and antibiotic charge density on LbL assembly was studied via evolution of dry film thickness. We found that the use of fluorinated PPz polyelectrolytes enhanced ionic pairing within LbL coatings, and that increasing charge density of small molecules increased antibiotic uptake. This strategy was successful even in the case of gentamicin, a hydrophilic, small antibiotic with only 3 to 4 positive charges at pH 7.5. Confirmation of antibiotic presence in films was demonstrated via x-ray photoelectron spectroscopy. Importantly, LbL films of fluorinated PPz polyelectrolytes retained antibiotics in physiological conditions due to the enhanced hydrophobic interactions. In contrast, LbL films of non-fluorinated PPzs released antibiotics at low pH and in the presence of salt following the charge renormalization argument. The potential of these coatings with a biomedically relevant bacterial strain, *Staphylococcus aureus*, is discussed.

COLL 158

Engineered functional amyloids as bionanomaterials: A synthetic biology approach

Ebru Sahin Kehribar, *ebru.sahin@bilkent.edu.tr*, **Musa E. Isilak**, **Ebuzer Kalyoncu**, **Urartu Ozgur Safak Seker**. *UNAM - National Nanotechnology Research Center, Bilkent University, Ankara, Turkey*

E. coli produces functional amyloid fibers in bacterial biofilms as highly ordered, complex and dynamic material systems that contribute to their adaptation to the environment, and increase their flexibility and functionality. In *E. coli*, there are two proteins as backbones of the nanofibers (CsgA and CsgB) in biofilms. CsgA is the major subunit responsible for seeding, as the minor subunit CsgB is responsible for nucleation. Bacterial amyloids are promising tools as bionanomaterials for many

functional applications. They are synthesized by well-defined machinery, readily form fiber networks covering large areas, and can be engineered for different functionalities. In our research, several cellular systems are designed to produce amyloid fibers with designed functionalities. Basic mechanisms and kinetics of nanofiber formation with differing compositions of purified CsgA and CsgB are investigated using QCM-D. The morphology of the fibers formed under different conditions were analyzed by SEM and AFM techniques. In addition to in vitro studies, in vivo morphological and mechanical properties of different amyloid fibers secreted from *E. coli* were characterized using AFM. Mechanical properties of biofilms as bio-nano interfaces could be tuned by controlling the secretion of amyloid fibers. In addition, electrically conductive protein nanofiber networks are developed. Conductive biofilms have the potential to act as interfaces between electrodes and bacterial populations. For this aim, CsgA fused peptides with aromatic aminoacids are constructed to contribute and alter the conductivity of the biofilms. The effect of different peptide motifs on the conductivity was characterized as the ohmic behavior of fibers on interdigitated electrodes. Currently, adhesive properties of amyloids are being studied in order to determine their potential as coating materials for cell adhesion. In addition to their intrinsic ability to adhere onto epithelial cells, it is also convenient to add peptide groups such as RGD to modify the bioadhesive properties of amyloids. In this aspect, we are coating glass surfaces with different combinations of purified native and modified biofilm proteins to investigate their activity as surface coating material for cell adhesion studies. Consequently, biofilm engineering for material science has promising applications through the genetically tunable biofabrication of self-assembling functional materials.

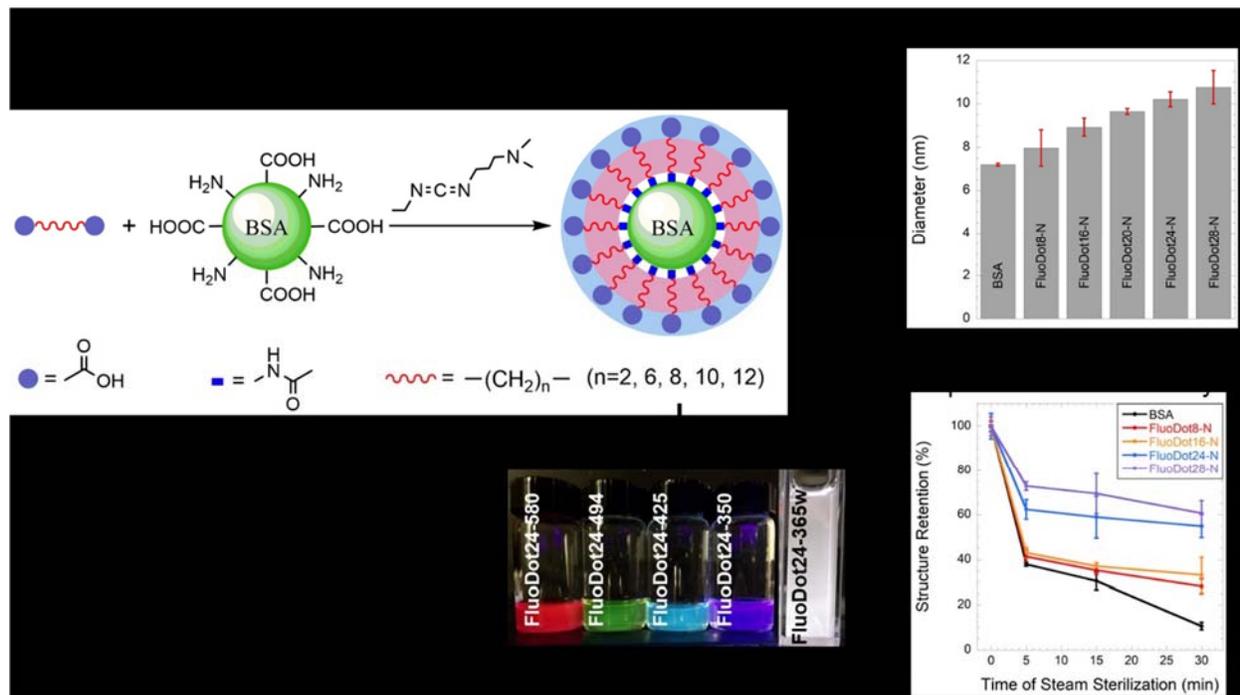
COLL 159

Fluorescent single protein nanoparticles with dimensions controlled at angstrom resolution and improved thermal stability

Jingwen Ding¹, jingwen.ding@uconn.edu, Jie He^{1,3}, Challa V. Kumar^{2,3}. (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (3) Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States

A novel kind of single protein nanoparticles (FluoDots) with tunable size are reported here, which have a central protein core surrounded by a covalently linked lipid layer. The size is tunable at 2.5 Å resolution with a sharp size distribution. These particles are negatively charged and FluoDots of increasing size have a similar charge. The FluoDots retain the structure of the protein embedded at the core of the particle, but have better thermal stability and a longer shelf time than the constituent protein. The most stable FluoDot retained 60% of the protein secondary structure after steam sterilization at 121 °C for 30 min. After labeling with specific fluorescent dyes, FluoDots emit different colors independent of their size, which is a major advantage over quantum dots. In addition, FluoDots that emit white light upon excitation at 366 nm are also produced and these are the first nanoparticle of their kind. FluoDots are water-soluble, non-toxic, biocompatible and biodegradable, and suitable for biological applications such as LED

coatings, cell imaging, solar cell applications, cancer drug delivery, and other biological applications.



COLL 160

pH mediated cell uptake of alkyl carboxylate functionalized Q β VLPs

Hamilton Lee, hlgoldeneyex@gmail.com, Jeremiah J. Gassensmith. Chemistry and Biochemistry, University of Texas at Dallas, Dallas, Texas, United States

The surface charge of nanoparticles is known to affect their uptake by cells. However, additional properties may mediate the cell uptake of nanoparticles, given that other properties of nanoparticles known to affect cell uptake such as size and shape are controlled for. We have discovered that conjugating hexanoic acid derivatives onto bacteriophage Q β virus-like particles (VLPs) largely inhibits their uptake by macrophages and HeLa cells. In addition, conjugating aryl carboxylate derivatives onto Q β did not have the same effect. Furthermore, we have designed Q β conjugate featuring a terminal hexanoic acid moiety connected by a hydrazone linker acting as a pH responsive switch. When the Q β conjugate is treated with mildly acidic conditions, the hydrazone linker undergoes hydrolysis resulting in the release of the terminal hexanoic acid moiety and allowing the uptake of the Q β conjugate by cells.

COLL 161

Modeling of magnetization in self-assembled magnetic nanocubes

Fnu Sanoj, *sanoj@uic.edu. Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States*

Monte Carlo simulations were used to study magnetic properties of thin layers of self-assembled (13 nm) iron oxides superparamagnetic nanocubes (SPM NC), which were experimentally prepared and investigated by our collaborators. The experiments reveal that these superstructures have large magnetic hysteresis at a low temperature of $T=5$ K, but no hysteresis at room temperature, for external magnetic fields pointing both along and orthogonal to the layers of self-assembled NCs. Our simulations reveal the conditions necessary for the observation of hysteresis in dependence on the NC density and self-assembly structure. We show magnetic arrangements of superdipoles in NCs layers with a different degree of disorder in dependence on the external field and system history.

COLL 162

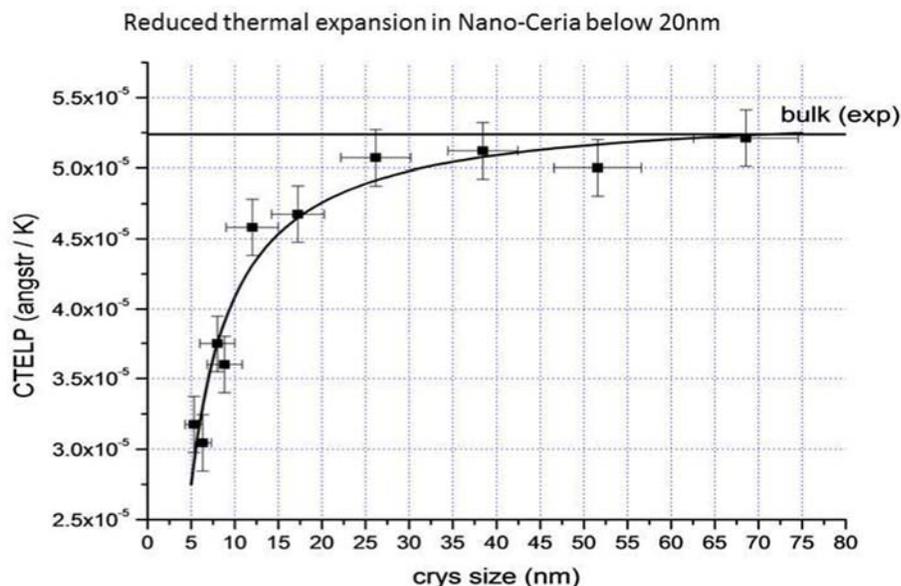
Crystallite-size dependent bond length, elastic and thermal properties of nano-oxides

Siu-Wai Chan, *sc174@columbia.edu. Applied Physics, Columbia University, NY, New York, United States*

When a lattice expansion of 0.1 to 0.5% as crystal-size decreases to ~ 5 nm suggest a negative surface stress in each of the five oxides: CeO_2 , MgO , Cu_2O , Fe_3O_4 , and Co_3O_4 . The finding is different from the positive surface stress observed in nanoparticles of noble metals. Surface stress is calculated from the amount of lattice-contraction as crystallite-size decreases. The present investigation is possible because of the mono-dispersed nature of the nano-oxide in each batch. We have also studied the pressure and thermal response of the lattice-parameter of nano-ceria and nano-MgO.

Hence, bulk modulus (B) and coefficient of lattice thermal expansion (α) were measured. Bulk modulus peaks around 33nm for nano-ceria and 14nm for nano-MgO. In both cases there is a quick decline below the peak. The findings have a number of implications for the bonding, surface-stress and elastic energy stored in the nanoparticles. Effects of surface adsorbents will be addressed with the help of earlier STM work on Fe_3O_4 (111) at Columbia University.

With binary oxides, the solubility of zirconia in nano-ceria is greater as the crystallite-size decreases and as the partial pressure of oxygen decreases. In reducing atmosphere, total solid solution in cubic fluorite structure is formed for full composition range of cerium and zirconium. Thus, the "bulk" phase diagram cannot predict the phases in nano-oxides. Even pure oxide of zirconium can be prepared in cubic fluorite structure with the right condition. Implication to their catalytic applications will be discussed. Cation valence change, and defect density will be discussed.



Materials Chemistry and Physics, 192, p. 311, (2017).

COLL 163

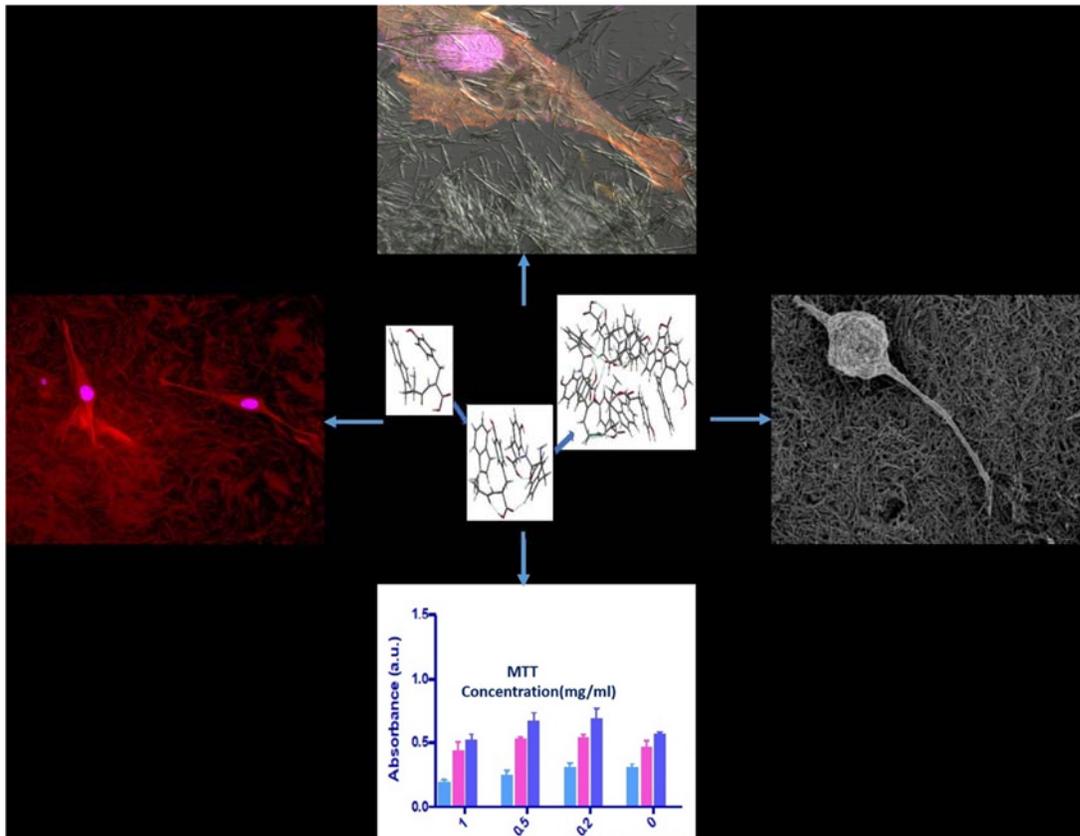
Synthesis and characterization of self-assembled peptide nanotubes: Scaffolds for neural cell differentiation

Prathyushakrishna Macha¹, pmacha@umassd.edu, Lisa Perreault¹, Milana Vasudev², Maricris Mayes¹. (1) Biochemistry, University of Massachusetts at Dartmouth, New Bedford, Massachusetts, United States (2) Bioengineering, University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States

Novel materials fabricated via self-assembly of biological molecules need to be both functional as well as biocompatible. Nanotubes composed of aromatic dipeptides dityrosine and tryptophan-tyrosine have been synthesized via solution-phase self-assembly (SPSA). Differential scanning calorimetry and thermogravimetric analysis were used to analyze the thermal behavior, whereas Fourier transform infrared spectroscopy, liquid chromatography-mass spectroscopy, and Raman scattering, and circular dichroism spectroscopy, and powder x-ray diffraction were used to analyze the chemical composition and secondary structure. Additionally, computational studies provided the mechanisms of interactions involved in self-assembly(Figure.1). Also, confocal and scanning electron microscopes(SEM) were used to study the morphological features of these nanotubes.

The cellular interactions and physiological effects of these SFSA nanotubes were examined using confocal microscopy, SEM, MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) and *in vitro* dopamine-enzyme linked immunosorbent assays on the rat adrenal pheochromocytoma cells (PC-12)(Figure.1), human cell-lines of M17 and SH-SY5Y. In order to understand their influence on dopamine and neural

differentiation genes using real-time polymerase chain reaction (RT-PCR). Similar studies with chemical vapor deposited nanotubes were performed to study the effects of nanotube scaffolds, especially neural differentiation.



COLL 164

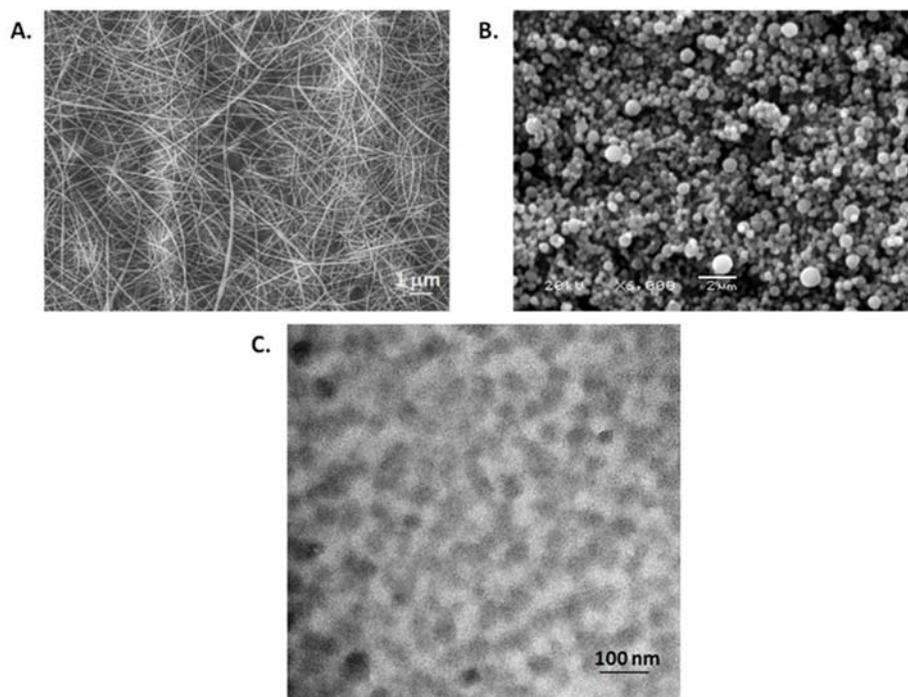
Peptide-based carriers for natural therapeutic molecules delivery

Yasaman Hamedani¹, yhamedani@umassd.edu, **Milana Vasudev**². (1) Bioengineering, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts, United States (2) Bioengineering, University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States

Biocompatibility, structural complementarity and biological recognition abilities are few of the properties of self-assembling peptides, which have contributed to various applications in regenerative medicine and targeted drug delivery. Non-covalent forces lead to peptide self-assembly specifically by π -stacking and hydrophobic interactions. Depending on the sequence of the peptides used for self-assembly, a vast range of nano-structures can be obtained like; nanofibers/spheres or micelles. In this study, various nanocarriers were evaluated for targeted delivery of natural compounds. The utilized oligopeptides are grouped into 2 categories: The 1st group of the oligopeptides form nanospheres/fibrous structures under electrostatic forces whereas the 2nd group are cationic, amphiphilic ones, which form micelles. These structures have the potential

of enhancing the drug delivery systems from several aspects such as; being responsive to the external stimuli like pH and presence of enzymes. In order to assess the influence of electrostatic forces on the assembly of biodegradable nanocarriers, several tests were performed, namely; Mass spectroscopy to study the chemical structure, FT-IR to study the secondary structure, DSC to study the thermal behavior.

Cranberry extracts have attracted considerable attention due to their antioxidative properties and inhibition of tumor cell proliferation. These natural compounds are grouped into 2 categories: Polar flavonoids such as quercetin and pro-anthocyanidins and nonpolar triterpenoids such as ursolic acid, both of which are unstable in biological environment and require a carrier for delivery to the tissues of interest. The aim of this work is to explore the fabrication of these nanocarriers, evaluate their ability of drug loading, release behavior and their biodistribution both *in vitro* and *in vivo* and their ability to inhibit tumor cell proliferation.



SEM images of A. Electrospun fibers of phe-tyr; B. Electrospayed tri-phe spheres; C. TEM image of peptide based micelles.

COLL 165

3D chiral microbuckles fabricated by asymmetric biaxial stretching

Myonghoo Hwang¹, audgn16@naver.com, **Changho Kim**², **Arum Jung**⁴, **Bomin Kim**³, **Bongjun Yeom**¹. (1) Hanyang university, Seoul, Korea (the Republic of) (2) Myongji university, Suwon, Korea (the Republic of) (3) Chemical engineering, Hanyang university, Seoul, Korea (the Republic of) (4) Hanyang University, Seoul, Korea (the Republic of)

Impart of chirality to artificial materials is great challenge in molecular scale to nano and micro scales. Previous research introduced complicated and sophisticated tools such as two photon lithography and e-beam technique for realization of chiral morphology in microscale. In this study, we utilized simple asymmetric in-planes stresses to fabricate microsized buckled patterns with 3D chiral morphologies. PDMS films were used for compliance substrates, and UV/Ozone treatments were applied to prepare asymmetrically pre-strained hard silicone oxide layers on top of the PDMS films. We investigated the effects of various conditions, such as UV/ozone treatment time, angle of strain directions, strain rate, and etc, to morphologies of micropatterns. This facile method can be extended to the manufacture of a large area pattern, and potentially applicable to advanced optical devices such as polarizing devices and holography.

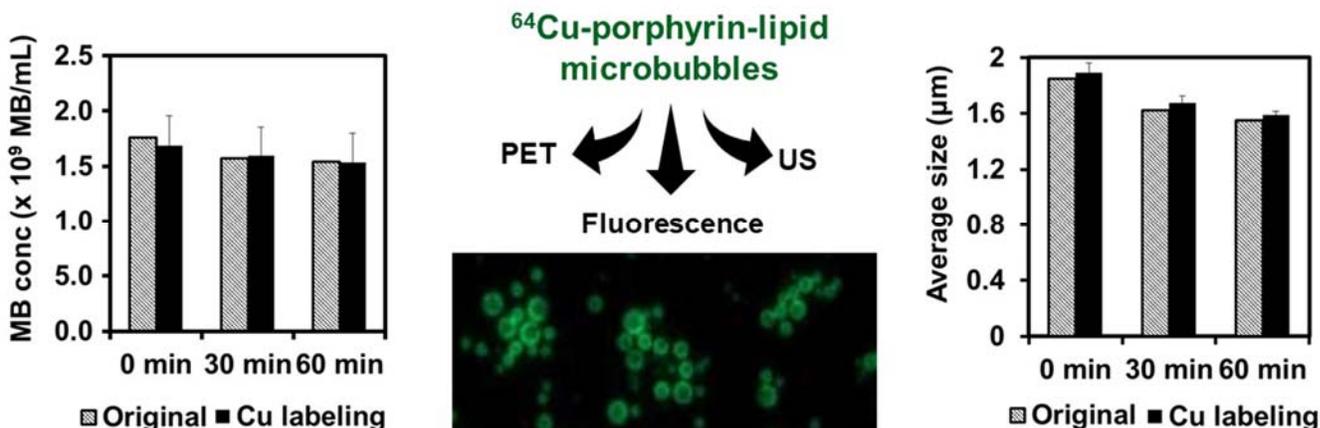
COLL 166

⁶⁴Cu chelation-enabled multimodal imaging of porphyrin-lipid micro and nanobubble shell fate: Applications in therapeutic ultrasound

Maneesha Rajora^{2,1}, maneesha.rajora@mail.utoronto.ca, **Juan Chen**², **Gang Zheng**^{2,1}. (1) University of Toronto, Toronto, Ontario, Canada (2) Princess Margaret Cancer Centre, Toronto, Ontario, Canada

The advent of therapeutic ultrasound (US) has extended the application of microbubbles from US imaging contrast agents to drug delivery vehicles able to breach intact vasculature, including the blood-brain barrier. These micron-sized agents are composed of a gaseous core, typically perfluorocarbon gas, encapsulated by a lipid, polymeric or protein shell. Despite their broad clinical and preclinical applications, characterization of microbubble shell fate both in the presence and absence of therapeutic US is limited. This is particularly pertinent for lipid microbubbles (the most widely used shell variant), which undergo an in-situ conversion in the presence of therapeutic US, generating nanoparticles that may no longer be confined to the intravascular space for clearance. Thus, given the increasing exploration of drug-loaded microbubbles, there is a need for chemical labeling strategies that enable quantitative and qualitative evaluation of microbubble and daughter nanobubble shell fate.

Here, we present a one-pot Cu-chelation strategy that generates multimodal porphyrin-lipid microbubbles (PMBs) amenable to fluorescence, positron emission tomography and US imaging of lipid microbubble shell fate. This rapid (30 min) metal chelation maintains PMB structure, size, stability and pharmacokinetic profile. It can be applied with high efficiency across microbubbles with varying lipid acyl chain lengths (C16 through C20) and porphyrin-lipid compositions. Furthermore, this chelation remains stable following sonication and conversion of the PMBs into nanoparticles, allowing for the first time, multimodal, longitudinal, and quantifiable imaging of both microbubble and daughter nanoparticle shell fate. Ultimately, the versatility and stability of our labeling strategy allows our results to apply to a diverse arsenal of lipid microbubbles, thereby broadly informing further development and application of microbubbles as theranostic drug delivery vehicles.



Rapid Cu-chelation of porphyrin-lipid shelled microbubbles generates multimodal particles with conserved size and stability

COLL 167

Study on changing rule of colloidal system properties in thermal cracking reactions

Jiguang Li, lijiguang.ripp@sinopec.com. Heavy Oil Processing, Beijing, China

The stability of the vacuum residue can be attributed to the colloidal stability of the vacuum residue system. Normally, asphaltene is considered as the solute of the colloidal system, and the maltene is considered as the solvent of the colloidal system for vacuum residue. The properties and quantities of solutes and solvents respectively determined the colloidal stability of the vacuum residue system.

In this paper, thermal cracking reactions of typical the Middle East vacuum residuum with different conversion conditions were studied. After reaction, the asphaltene and maltene of the reacting system were separated by standard method, and then the elemental composition, molecular weight, NMR and IR of asphaltene and solute were analyzed respectively. Through the experimental results, we can see that not only the amount of asphaltenes and maltenes but also their properties and compatibility determined the stability of the colloidal system for examined Middle East vacuum residue.

COLL 168

Structure and dynamics of aqueous solutions containing poly-(acrylic acid) and non-ionic surfactant: A comparative study between pentaethylene glycol n-octyl ether (C_8E_5) and octaethylene glycol n-decyl ether (C_{10}E_8)

Lakshmikummar Kunche, Upendra Natarajan, unatarajan@iitm.ac.in. Indian Institute of Technology (IIT), Chennai, India

We present the first computational (molecular level) study of aggregation in a chemically real polymer-non-ionic surfactant-water system. Previous related studies have looked at surfactant self-assembly in aqueous solution. Atomistic MD simulations were carried out to study intermolecular structure and thermodynamics of solvation in an aqueous solution containing C₈E₅ and C₁₀E₈ separately with uncharged poly(acrylic acid) PAA. The concentration of surfactant (C_s) was varied in the range 0.01–0.3 M (dilute to concentrated) while polymer concentration (C_p) was kept in the dilute condition (i.e. $C_p=0.01$ M). The binary (surfactant, water) and ternary (polymer, surfactant, water) systems show random non-uniform (RNU) micellar-like aggregates at low C_s and lamellar aggregates at high C_s . The transition from RNU micelle phase to lamellar phase in the ternary system occurs at lower C_s for C₁₀E₈ as compared to C₈E₅, whereas this transition in the binary systems occurs at lower C_s for C₈E₅ than C₁₀E₈. The interaction and binding between PAA and surfactants takes place at low C_s suggesting strong intermolecular interaction, in agreement with experimental data [1]. For lamellar aggregates the adsorption of PAA chain on to the aggregate shows favorable interaction between -COOH groups of PAA and -C-O- groups of the surfactant. PAA absorbs as a coiled chain at low C_s (RNU micelle) and as a stretched chain at high C_s (lamellar phase). In the C₁₀E₈ binary systems micelles form at lower values of C_s indicating a decrease in CMC with increase in hydrophobic tail length, in good agreement with experimental data. Symmetric lamellar aggregates are formed in the C₈E₅ system at higher C_s and are absent in the C₁₀E₈ system. The RNU micelles formed in both surfactant systems were approximately spherical. SASA of the aggregates was high in binary systems as compared to the respective ternary systems, for both surfactants, which indicates polymer chain absorbed on the surface of the aggregate instead of penetrating the hydrophobic core. These results were analyzed using radial distribution functions (RDF). Solvation enthalpy of binary and ternary systems becomes more exothermic with increase in C_s indicating a strong favorable interaction between surfactant and polymer. Detailed analysis of hydrogen bonding and atom density profiles was carried out and results will be presented.

COLL 169

Evolution of bioinspired self-assembled materials in nucleic acid therapeutics and vaccines

Marian Gindy, marian_gindy@merck.com, Andrew Bett, Gokul Swaminathan, Jeffrey Smith, Susan Secore, Andrew Latham, Manishkumar Patel. Merck Research Labs, Merck and Co, Inc, Rahway, New Jersey, United States

Biological molecules form intricate and precise architectures with characteristic dimensions and structural features spanning from the nanoscale to the macroscale. This level of precision confers highly dynamic, multi-functional and complex biological functions. New synthetic materials, designed to achieve structural or chemical diversity in three dimensions, have the potential to recapitulate desired biological functions, marrying the specificity of natural biomolecules with the control of synthetic material systems. Such self-assembled materials have the potential to impact numerous

applications in drug design and delivery. In this work, we discuss emerging evidence demonstrating the utility of novel engineered lipid nanoparticles for delivery of nucleic acids and as immunomodulatory agents in the context of viral and oncological vaccines and therapeutics.

COLL 170

High resolution nanoparticle sizing with Maximum A posteriori nanoparticle tracking analysis (MANTA)

Kevin Silmore, silmore@mit.edu, Xun Gong, Michael Strano, James Swan. Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Unbiased estimation of nanoparticle size distributions remains a challenge affecting numerous fields including nanotechnology and biopharmaceuticals. Current methods for particle sizing, such as dynamic light scattering, analytical ultracentrifugation, and field-flow fractionation, can suffer from a combination of intensity biases, difficult sample preparation, insufficient sampling, and ill-posed data analysis. The last issue, ill-posedness of the governing equations for these particle sizing techniques, guarantees that noise in the data will make reproducible measurements impossible without aggressive regularization. We have developed a new Bayesian method, Maximum A posteriori Nanoparticle Tracking Analysis (MANTA), for estimating the size distributions of nanoparticle samples from high-throughput single particle tracking experiments. In this method, unbiased statistical models are derived for two observable quantities in a typical nanoparticle trajectory - the mean squared displacement and the trajectory length - as a function of the particle size, finite elements are used to discretize the particle size distribution, the weights of the finite elements are found via MAP estimation, and robust cross validation is applied to mildly regularize solutions to the MAP problem. MANTA infers nanoparticle size distributions with unprecedented resolution. The precision of the method is assessed by performing extensive Brownian dynamics simulations with synthetic particle size distributions that are known exactly. In experimental testing with gold nanoparticles, MANTA is capable of reliably resolving disparate populations of particles with relative variation in size as small as 30%.

COLL 171

Particle size distribution of food additives: Silicon dioxide study

Sadia A. Khan, sadia.afarin.khan@gmail.com, Timothy R. Croley. U.S. Food and Drug Administration, College Park, Maryland, United States

In 2006, the U.S. Food and Drug Administration (FDA) initiated a Nanotechnology Task Force (NTF) to address the regulatory concerns associated with the use of nanoscale materials in FDA-regulated products. Silicon dioxide in its amorphous form, a white metal oxide, is an approved food additive in the United States. It has been used as an

anticaking agent in powdered food products, a chill proofing agent in malt beverages, and a filter aid in wines, beer, and juices for many years. During production, there is the possibility of nanoscale silicon dioxide particles to occur in food additives; however, there are currently no data on the particle size distribution of food additive silicon dioxide. In line with the NTF, we characterized and analyzed the particle size distribution of commercially available food-grade silicon dioxide using Transmission Electron Microscopy (TEM), Field Effect Scanning Electron Microscopy (SEM), and Dynamic Light Scattering (DLS) assay. These data serve as a foundation to address potential regulatory concerns as well as an assessment of the current state of these types of food additives.

COLL 172

Particle sizing of a food supplement in response to an EFSA request for characterization of potential nanomaterials

Robert I. Maccuspie, *rob@n-icorp.com*. Natural Immunogenics Corp., Sarasota, Florida, United States

This presentation will focus on recent particle sizing techniques used to support a request from the European Food Safety Administration for particle size characterization as they determine whether there is a potential for the presence of nanomaterials in a dietary supplement. Regulatory guidance documents require Transmission Electron Microscopy and one additional sizing technique. A brief discussion of why Atomic Force Microscopy was selected as the most appropriate metrological technique for this application will include meeting regulatory compliance needs as well as operational quality control laboratory demands such as cost and analysis time. A summary of the development of the performance qualification of the methods, instruments, and software will be presented. Finally, a summary of the data from the measurement of over 60,000 particles by TEM and over 3,000 particles by AFM will be presented, demonstrating a comprehensive understanding of the particle size distribution of the product.

COLL 173

General way to synthesize Sm-based nanomagnet

Bo Shen, *bo_shen@brown.edu*, Shouheng Sun. Brown University, Providence, Rhode Island, United States

Developing permanent nanomagnets is a critical step to maximize the magnetic performance for miniaturization of electronic and magnetic devices. Among various permanent magnets, Sm-based nanomagnet (SmCo_5 $\text{Sm}_2\text{Co}_{17}$ $\text{Sm}_2\text{Fe}_{17}\text{N}_3$) is a class of the most promising materials due to its large coercivity and high Curie temperature. However, the synthesis of Sm-based nanomagnet is very challenging due to a high reduction potential of Sm^{3+} (-2.3V). Previous chemical synthesis of reducing SmCo-OH cannot control the size of nanoscale SmCo_5 , which decreases their magnetic

performance. Herein, we report a new chemical strategy of SmCo₅ nanoparticles (NPs) synthesis. The size of particles can be adjusted from 50 nm to 200 nm with good control. First, we prepared 100 nm flower shape SmCoO NPs from organic solution by thermal decomposition of Sm(acac)₃ and Co(acac)₃ (acac=acetoacetate). After a calcium oxide coating and high temperature (850°C) reductive annealing, 100 nm crystalline SmCo₅ NPs were obtained with a coercivity of 31kOe. By changing the concentration of Sm and Co precursor, 50 nm and 200 nm SmCo₅ NPs can also be obtained. By simply adjusting the ratio of Sm(acac)₃ to Co(acac)₃, pure hexagonal-structured Sm₂Co₁₇ NPs can be synthesized. If the Co(acac)₃ precursor was replaced by Fe(acac)₃, Sm₂Fe₁₇ NPs were obtained and further can be nitrogenized to Sm₂Fe₁₇N₃. The method provides a general synthesis route of high-performance Sm-based nanomagnet.

COLL 174

Cation distribution in composite quantum dots prepared by partial cation exchange

*Chen Lin, Savannah E. Benjamin, Hailey D. Hall, Mackenzie L. Ary, Xyan A. Aguilar, Johnathan W. Campbell, **Paul G. Van Patten**, greg.vanpatten@mtsu.edu. Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee, United States*

Cation exchange (CE) reactions offer avenues to new types of nanostructures, and under the right conditions, partial CE may even provide routes to novel nanoheterostructures. Partial CE may also provide routes to known nanoheterostructures using conditions that are milder or otherwise superior to the established methods. In order to attain these benefits of CE it is first necessary to develop an understanding of how cations are distributed in the daughter nanocrystals produced via CE. Here we present results from recent and ongoing studies concerning the distribution of metal cations following CE reactions in which only a portion of the cations in the initial QDs are exchanged. Structural features of the daughter particles have been studied via powder x-ray diffraction (PXRD), transmission electron microscopy (TEM), and high-resolution scanning transmission electron microscopy with energy-dispersive spectroscopy (STEM-EDS) to map elemental distribution within particles at near atomic scale.

COLL 175

New method of comparing photocatalysts by identifying reaction intermediates

***Mark Croxall**, mark.croxall@mail.utoronto.ca, M. Cynthia Goh. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada*

Photocatalysis has been explored as a potential method of cleaning wastewater but most studies of photocatalytic efficacy rely on the disappearance of colour of dyes.

Ideally, the breakdown would result in non-toxic materials, but there is little study done, and the intermediates of this photocatalytic process are not well understood, and could potentially result in the accumulation of more dangerous intermediate. In order to track these intermediates, Nuclear Magnetic Resonance spectroscopy (NMR) has been used as a probe for identification of possible intermediates and their persistence using TiO₂ & BiOCl as photocatalysts. Liquid Chromatography Mass Spectrometry (LC-MS) experiments were used in conjunction with NMR to explore the mechanism and identification of previously unknown intermediates in the degradation of naproxen, a non-steroidal anti-inflammatory drug (NSAID).

COLL 176

Acceleration of photoisomerization reaction of lophine dimers with inner environment of the micelles

Masaaki Akamatsu¹, makamatsu@rs.tus.ac.jp, Kazuki Kobayashi¹, Taiki Suzuki¹, Kenichi Sakai^{1,2}, Hideki Sakai^{1,2}. (1) Tokyo University of Science, Chiba, Japan (2) Research Institute for Science and Technology, Tokyo University of Science, Chiba, Japan

A lophine dimer (LPD), that is one of the photochromic compounds, is cleaved into a pair of colorized lophyl radicals by ultraviolet (UV) light irradiation. The radical species reversibly recover to the colorless lophine dimer by thermal recombination. In comparison with the rapid coloration reaction by the UV irradiation, the thermal decoloration reaction is extremely slow because low collision frequency for recombination caused by the free diffusion of the radicals in solution. Recently, Abe and coworkers reported lophine dimers with a linker showed rapid recombination reaction. In this study, we tried to accelerate a recombination reaction of the lophyl radicals by using the inner environment of the micelles, spontaneously formed by surfactants. In this presentation, we will discuss the effects of the solubilization state of lophine dimers in the micelles and the chemical structures on the speeds of the recombination reaction of the lophyl radicals.

COLL 177

Adsorption of amino acids onto TiO₂ nanoparticles: Towards understanding nano–bio interactions

Natalia I. Gonzalez Pech¹, nig011@ucsd.edu, Irem Ustunoğlu², Haibin Wu¹, Brian Kenney¹, Vicki H. Grassian¹. (1) Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States (2) Nanoengineering, University of California, San Diego, La Jolla, California, United States

Nanoparticles in biological media adsorb proteins onto their surface and generate protein coronas. The protein affinity toward nanoparticle surfaces potentially depends on the constituent amino acid side chains which are exposed to the solution and

available for interaction. Therefore, studying the adsorption of individual amino acids on nanoparticle surfaces can provide valuable insights into the overall evolution of the protein corona. In the current study, the surface adsorption of several amino acids on TiO₂ nanoparticles at different pHs is studied from both macroscopic and molecular perspectives. ATR-FTIR spectroscopy and QCM-D analysis are used to determine and quantify adsorption mechanisms.

COLL 178

Affinity chromatography measurements of metal ion binding to lipid membranes

Eric E. Ross, rosse@gonzaga.edu. Gonzaga University, Spokane, Washington, United States

Metal ions interact over a range of affinities and specificity with biomembranes. The interaction affects many properties and functions of lipid bilayers and associated biomolecules. Measurement and characterization of ion binding to lipids is often difficult owing to the low affinity of the interaction and the analytical complications associated with dynamic and polydisperse liposome structures. This presentation describes the use of colloid-supported lipid bilayers as stationary phases for affinity chromatography measurements of ion binding to lipids and bilayer-embedded ionophores. The operational parameters and material development of the colloidal stationary phases are explained, and data highlighting the critical factor that the support structure plays in measuring lipid phase-sensitive binding interactions are shown. Results for group II ions binding to different lipid classes and group I ions binding to membrane ionophores are presented, and a comparison is made to values determined using other techniques where available. Chromatography provides a direct measure of affinity and enables measurements under physiologically relevant conditions. This work describes our current understanding of the potential and limitations of the methodology for the study of ion-binding at lipid membranes.

COLL 179

Aggregation process of amyloidogenic peptides coated nano-gold colloidal particles

Ishan Deshmukh¹, ishan.deshmukh@gmail.com, Joseph Lippa², Kazushige Yokoyama². (1) Biochemistry, SUNY Geneseo, Geneseo, New York, United States (2) Chemistry, The State University of New York Geneseo College, Rochester, New York, United States

The aggregation process of amyloidogenic peptides coated nano-gold colloids was investigated under pH 4 and below. The amyloidogenic peptides studied in this work were amyloid beta 1-40 (Ab₁₋₄₀), alpha-synuclein (α-syn), and beta 2 microglobulin (b2M), and they were coated over nano-gold colloidal particles ranging between 10nm and 100 nm. Under relatively high acidic condition, all studied amyloidogenic peptides

exhibited an unfolded peptide structure with hydrophilic segment exposed toward outside and hydrophilic segment used as an adsorption anchor over the nano gold surface. Thus, the hydrophilic segments were speculated to be used for an interaction between amyloidogenic peptide coated nano-gold colloid. The spectroscopic inspection extracted the critical pH point (pH_0) at where the color change of the amyloidogenic peptide coated nano-gold colloids due to an occurrence of an aggregation of nano-gold colloid particles. With a combination of TEM (Transmission Electron Microscopy) and the geometric simulation, it was concluded that prolate shaped peptides cross each other conforming a multiple layer over each nano gold surface. The unfold peptides were considered to be interacting with charge-charge interaction over the nano gold surfaces.

COLL 180

Amino acid homology of peptide sequence as a determining factor in single pot reduction of Au nanoparticles

*Catherine J. Munro*¹, *catherine.munro.90@gmail.com*, *Marc R. Knecht*². (1) *Chemistry, University of Miami, Miami, Florida, United States* (2) *Dept of Chemistry, Univ of Miami, Coral Gables, Florida, United States*

Nanoparticles and bottom-up synthesis techniques of materials often involve exogenous reagents that do not end up incorporated into the final material. This includes the traditional peptide-mediated gold material synthesis where sodium borohydride is added after peptide ion complexation time. Recent advances in peptide-mediated gold materials have shown that Au binding peptides like AuBP1 (WAGAKRLVLRRE) and AuBP2 (WALRRSIRRQSY) have the capacity to eliminate all exogenous reagents to generate colloidal suspensions where the non-covalent interactions of the peptide modulate the properties of the material at the abiotic/biotic interface. These studies identify that the position of the tryptophan residue in the sequence, as well as the pH of the aqueous solution and ions present in solution all, effect the rate of material reduction. Tryptophan is a relevant reducing agent for the synthesis of peptide-mediated gold nanoparticles, but can tryptophan be appended to non-gold specific peptides to induce the reduction of Au^{3+} to Au^0 ? Here in we present the effects of peptide sequence homology on the reduction capacity of Au^{3+} to Au^0 where the localized surface plasmon resonance was tracked for over time. Additionally, fluorescence quenching studies of these tryptophan mutated non-Au specific peptides were used to study how the sequence and binding affinity of the mutated peptide may correlate to the rate of reduction observed in the time-resolved plasmon. Finally, transmission electron microscopy (TEM) was performed to identify how the homology of the peptide sequence effects the final material morphology. Collectively, these results show that the entire peptide works in concert to control the reduction process of the Au material and that the sequence of the peptide is important to how the tryptophan residue will react in the presence of Au^{3+} . By advancing the understanding of the conditions required for a biomimetic reduction process of Au materials, an evolution in material design may be possible.

COLL 181

Efficient route to amine functionalized siloxy gels

Bhanu P. Chauhan, *chauhan.cepm@gmail.com*, **Gurpreet Longia**, *longiag@student.wpunj.edu*. Department of Chemistry, William Patterson University, Wayne, New Jersey, United States

Well-defined functional silicon based gels are materials of high importance due to their wide-ranging applications particularly in industrial setting. We are interested in devising the tailor made gels, which will find applications as catalysts for various organic transformations. In particular, we are interested in creating functional silicon based platforms, which will not only act as catalysts but also provide recyclability properties.

In this presentation, we will describe a synthetic protocol in which amine functionalized siloxy gels are synthesized in a one step process. The silane is prepared via the reaction with nitrate salts saturated with a Bis(trimethoxysilylpropyl) and N-halosuccinimide (NXS) forming a porous gel. The Bis(trimethoxysilylpropyl)amine is hydrolyzed in a presence of polar protic solvents and the halosuccinamides were added to the reaction mixtures as catalyst. Generated materials exhibited a porous framework with metal complexed within. These materials were able to maintain their amino moieties for further chemical applications. Structural and spectroscopic analysis of these samples was carried out by; ^{29}Si NMR, ^{13}C NMR, ^1H NMR, TEM, SEM/EDX, TGA, FT-IR and Raman techniques.

COLL 182

Analyzing the roles of surfactant mixtures containing aromatic additives and hexadecyltrimethylammonium chloride in the synthesis of gold nanorods

Iris W. Guo, *iguo@sfu.ca*, **Byron D. Gates**. Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada

Gold nanorods have been extensively studied to finely control their shape and tune their aspect ratio with the goal of better understanding their growth mechanism and obtaining products with well-controlled and well-defined optical properties. This understanding and ability to control their properties are also important for the use of gold nanorods in a variety of applications that include plasmonic materials, photothermal therapy, and catalysis. Seed-mediated solution phase synthesis is one of the most widely used methods to prepare gold nanorods. Recently, the use of additives and/or binary surfactant systems have been reported to be effective in achieving a more precise regulation of aspect ratio, as well as minimizing by-products compared to methods that use a single surfactant to regulate the growth of the nanorods. The study presented here provides a further investigation into the role of additives on the synthesis of gold nanorods. As one example, a systematic investigation is presented on a reaction mixture containing surfactants hexadecyltrimethylammonium bromide along with

hexadecyltrimethylammonium chloride and one or multiple types of aromatic derivatives of salicylic acid. The resulting gold nanorods were characterized through a combination of extinction spectroscopy, particle size analyses, and electron microscopy techniques. The results of this correlative analysis reveal further insights to the roles of surfactants and additives, as well as their interactions with other chemical species in the growth solution and their influence on the formation of gold nanorods. These results also serve to gain a more detailed insight into controlling seed-mediated methods to reproducibly achieve gold nanorods of a desired size and uniformity.

COLL 183

Antimicrobial carbohydrate-passivated gold nanoclusters

Will Ndugire, william_ndugire@student.uml.edu, Mingdi Yan. Dept of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States

As public health concerns continue to grow about the scale and pace of antimicrobial resistance, alternative strategies and materials are needed. In this aspect, inorganic nanoparticles are increasingly studied as potential alternative antibacterial agents. One such material is colloidal gold nanoparticles. Large gold nanoparticles (> 2 nm) are mostly utilized as drug delivery vectors as they are biologically inert. On the other hand, smaller (< 2 nm) gold nanoclusters (AuNC) have shown promising antimicrobial activity particularly against Gram-positive bacteria. Due to their size, AuNC show a dualism in properties between organo-gold complexes and colloidal nanoparticles - for instance sharing a defined stoichiometric formula with the former, and having an inner core/passivating ligand shell structure typical of the latter. However, attempts to apply these clusters in antibacterial use have not been straightforward due to their noted toxicity to mammalian cells. To combat this, we present an approach modulating toxicity using carbohydrates. The synthesis and characterization of these new AuNCs will be presented, together with the antimicrobial activities against Gram-positive as well as Gram-negative bacteria. The cytotoxicity of these AuNCs will be evaluated using a hemolytic assay and on human lung cancer cells.

COLL 184

Application of gold-silica core-shell nanostructures to treat glioblastoma associated with NHE9 overexpression

Lena Juratli, ljuratli@umich.edu, Sarah Nasser, Ashley Pall, apall@umich.edu, Kalyan C. Kondapalli, Krisanu Bandyopadhyay. Department of Natural Sciences, University of Michigan - Dearborn, Dearborn, Michigan, United States

Glioblastoma multiformae (GBM) is the most aggressive type of malignant brain tumor with complex molecular profile. In subsets of GBM, increased expression of Na⁺/H⁺ exchanger, NHE9, is a potent driver of tumor progression and is associated with decreased patient survival. In glia, NHE9 is localized to sorting endosomes where it

regulates endosomal pH by transporting luminal protons out in exchange for sodium or potassium ions. Overexpression of NHE9 alkalinizes the sorting endosomes and attenuates turnover of epidermal growth factor receptors (EGFRs) thereby increasing persistence of EGFRs on the plasma membrane. EGFR signaling regulates multiple cellular functions including cell growth and division. Downregulation of NHE9 acidifies sorting endosomes limiting EGFR trafficking to the glioblastoma cell membrane and is a potential therapeutic strategy for glioblastomas with NHE9 overexpression. We are conducting pilot studies of a trimodal therapeutic approach, in cell culture experiments. Gold nanoshell-enabled photothermal therapy (NEPTT) is emerging as a promising platform for cancer treatment. Silica-core/gold-shell nanoparticles can absorb radiation in the 700-900 nm range to target cancer cells while leaving the surrounding, healthy tissue unharmed. We have successfully synthesized gold nano-shells on ~200 diameters silica cores. It is observed that endocytic uptake of gold nanoshells is elevated in glioblastoma cells that overexpress NHE9. Herein, we report results from the effects of combinatorial approach using NHE9 downregulation, tyrosine kinase inhibition and NEPTT on glioblastoma cell proliferation.

COLL 185

Atomic resolution 3D reconstruction of single colloidal nanoparticle

Junyoung Heo, hgy3927@snu.ac.kr, Byung Hyo Kim, Sungin Kim, Jungwon Park. School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of)

Understanding structure of nanoparticles is important because their structures determine physical, chemical, and catalytic properties. However, there is no right tool to map 3D structures of nanoparticles with details of atomic positions in the native liquid condition. Our method based on high-resolution liquid cell TEM has been developed to reconstruct the 3D structures of colloidal nanoparticles. When Pt nanoparticles are immersed in graphene liquid cell, the freely rotating nanoparticles can be observed by high-resolution TEM. A time-series TEM images capture two-dimensional projections of the rotating particle from different directions. Using reconstruction algorithm, 2D projections can be merged to 3D structure map of individual nanoparticle with angstrom spatial resolution. Obtained 3D density maps unveil face-centered cubic structures Pt nanoparticles with distortions, grain boundaries, and strains applied along particular directions.

We observe individual particles have different morphologies and internal structures with respect to the assembly of constituent elements. With high-resolution 3D density maps with atomic positions assigned, local strain and the volume occupied by individual elements are investigated for nanoparticles with different size.

COLL 186

Biodegradable tetra-block copolymeric nanoparticles for MS1 anti-cancer peptide delivery

Neha Mehrotra¹, *mehrotra.neha.93@gmail.com*, **Dikshi Gupta**¹, **Surender Kharbanda**², **Harpal Singh**¹. (1) Center for Biomedical Engineering, Indian Institute of Technology Delhi, New Delhi, National Capital Region, India (2) Dana Farber Cancer Institute, Harvard Medical School, Boston, Massachusetts, United States

Mcl-1 is an anti-apoptotic protein of the Bcl-2 family and is overexpressed in a variety of human cancer types including breast, CNS, colon, lung, ovarian, prostate, leukemia and melanoma. MS1, an anticancer peptide which selectively binds to Mcl-1 has been reported to prevent its dysregulation. Peptide therapy has limited success in cancer therapeutics due to its low bioavailability, potential immunogenicity and poor metabolic stability. A biodegradable polymeric nanocarrier based strategy has been proposed to improve peptide stability and bioavailability. In the present work, PLA-PEG-PPG-PEG based tetra block copolymeric nanoparticles were designed and developed to efficiently encapsulate and deliver MS1 peptide. The hydrophilic peptide loaded nanoparticles were synthesized by double emulsion solvent evaporation method and showed an encapsulation efficiency of 86%. The MS1 loaded biodegradable nanoparticles had an average diameter of 166 nm with a zeta potential of -13mV. Further characterization of MS1 loaded NPs by FE-SEM and TEM, showed spherical morphology with uniform size distribution. MS1 NPs showed an initial burst release of 14% in 24 h followed by a sustained release upto 30 days. Studies on cellular uptake by CLSM and cytotoxicity assays of the blank polymeric nanoparticles, demonstrated that the nanoparticles were effectively taken up by the cells and showed good biocompatibility. The MS1 loaded NPs showed efficient cell proliferation inhibition, with an IC₅₀ of 48nM in MCF-7 breast cancer cells and an IC₅₀ of 840nM in THP-1 AML cells. The MS1 peptide was further co-encapsulated with chemotherapeutic drug paclitaxel in the polymeric nanoparticles to explore the potential for synergistic effect. On co-encapsulation, MS1 and paclitaxel showed an encapsulation efficiency of 90% and 95% respectively. The dual loaded nanoparticles showed an average diameter of 197nm with a zeta potential of -18.9mV. The dual loaded NPs showed an IC₅₀ value of 0.06nM in MCF-7 cells, significantly lower than that of single loaded MS1 or paclitaxel NPs. The PLA based tetra block copolymer nanoparticles reported in the present study show high loading efficiency, sustained release, good biocompatibility and therefore have high potential for delivery of anticancer peptides alone or in combination with conventional chemotherapeutic drugs for cancer therapy.

COLL 187

Bio-functionalization of graphene oxide for antimicrobial and drug delivery applications

Ipsita A. Banerjee¹, **Mindy Hugo**¹, *mhugo1@fordham.edu*, **Karl R. Fath**². (1) Department of Chemistry, Fordham University, Rego Park, New York, United States (2) Biology, CUNY, Queens College, Flushing, New York, United States

Composites of graphene oxide (GO) were developed to reduce toxicity and enhance biological applications. In order to achieve this, GO was first covalently attached to

specific amino acid protected linkers, including lysine or phenylalanine or tryptophan. After confirmation of attachment spectroscopically, the composites were then further attached to phytochemicals and specific phytochemicals to impart biocompatibility as well as anti-inflammatory properties. The formed composites were then used for encapsulation of topoisomerase inhibitors. The formed product was employed as a drug release device in vitro. The cytotoxic effects of the constructs, as well as their capability to bind to breast cancer cells were examined. Additionally, the mechanism of induced cytotoxicity was studied. Electron microscopy was used to examine the morphologies of the assemblies and the formation of the composites was confirmed by FTIR and UV-VIS spectroscopy. Furthermore, the antimicrobial activity against E-Coli was also examined.

COLL 188

Biopolymer functionalized liposomes for enhanced dispersion stability of nanovesicles

Lindsey Hyppolite, lhyppolite09@students.desu.edu, Cherese Winstead Casson. Chemistry, Delaware State University, Dover, Delaware, United States

Liposomal nanoparticles are essential in the delivery of chemotherapeutic drugs. The development of an ideal liposomal nanoparticle drug delivery system is of increasing interest to ensure that the conjugated drug carrier complex arrives and acts preferentially at the tumor site with high efficacy and lower toxicity. The focus of this work lies in the synthesis of functionalized liposomal nanoparticles with the biopolymer chitosan (CS) to enhance the stability nanoparticle dispersion. Characterization of the liposome vehicles were studied using Fourier Transform Infrared Spectroscopy (FTIR), zeta potential analysis, particle size analysis (PSA), and scanning electron microscopy (SEM). Preliminary findings in the characterization of the synthesized liposomes using FTIR showed characteristic bands at 3429 cm^{-1} due to -OH and -NH groups in chitosan and 1656 cm^{-1} amide band C-O stretching, along with N-H deformation. Structural characteristics of the synthesized liposomes were also studied by dynamic light scattering. The liposome suspensions presented exhibited mean diameters between 150 nm and 250 nm, polydispersity indexes (PDI) around 0.4, zeta potential values between -40 mV and -30 mV, indicating complex formation between the anionic liposomes and cationic chitosan molecules. The surface morphology of the nanovesicles were studied using scanning electron microscopy and it was observed that the liposomes are uniform in diameter (~190nm) with unilamellar structures. XRD analysis exhibited diffraction peaks corresponding to chitosan functionalization occurring at 20° 2 theta. Stability studies of the functionalized CS-liposomes showed increased stability to aggregation versus pristine liposomes when stored at ambient temperatures.

COLL 189

Blood protein interaction with nanostructured glycolyx mimetic surfaces

Mohammadhasan Hedayati¹, *hedayati.che@gmail.com*, **Melissa M. Reynolds**², **Diego Krapf**³, **Matt Kipper**⁴. (1) *Colorado State University, Fort Collins, Colorado, United States* (2) *Chemistry Department, Colorado State University, Fort Collins, Colorado, United States* (4) *Dept of Chem Biol Engineering, Colorado State University, Fort Collins, Colorado, United States*

There is currently no engineering material used in cardiovascular implants and devices that completely prevents blood clotting when in long-term contact with flowing whole blood. Considering implantable biomaterials and devices, adsorption of nonspecific proteins, such as albumin, fibrinogen, and von Willebrand factor, can be a particularly undesirable event, which can lead to biological responses such as coagulation, thrombosis, and bacterial infection.

The dominant approach to developing next-generation blood-compatible surfaces is to design surface chemistries and structures that reduce or eliminate protein adsorption to prevent blood clotting. This work proposes a new paradigm for developing blood-contacting surfaces by strategically mimicking key features of the inside surfaces of blood vessels: negatively charged glycosaminoglycans organized into a polymer brush with nanoscale domains. The interactions of blood proteins with glycocalyx mimics are revealed in detail using single-molecule video microscopy. This novel approach shows for the first time that the nanoscale structure and organization of glycosaminoglycans in the glycocalyx is essential to (i) reduce protein adsorption, (ii) reversibly bind fibrinogen, and (iii) suppress fibrin polymerization. This work reveals a previously unknown mechanism whereby the endothelial glycocalyx prevents blood clotting that can be exploited for the design of blood-compatible materials.

COLL 190

Characterization of surface chemical processes during the leaching of silver from a polymetallic sulfide by x-ray photoelectron spectroscopy and polarization microscopy

Dhamelyz Silva Quiñones¹, *dhalyz.silva@gmail.com*, **Juan C. Rodriguez-Reyes**¹, **Andrew V. Teplyakov**², *River He*². (1) *Bioengineering and Chemical Engineering, UTEC, Lima, Lima, Peru* (2) *Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States*

Mineral processing has evolved to become a vibrant research area where the ores become progressively more complex and with lower concentration of valuable metals. Therefore, new strategies for understanding the behavior of minerals composing an ore are actively sought. This study focuses on understanding surface processes occurring during the cyanide leaching of a complex polymetallic sulfide containing silver from the Central Andes of Peru. Through the combination of polarization microscopy and X-ray photoelectron spectroscopy (XPS) it is possible to obtain information of the leaching process at different stages. Approximately 30% of the silver is extracted through cyanide leaching, and the rest is encapsulated in different minerals, as it can be deduced from EDX analysis. Surface analysis of fresh and leached samples with XPS

show the gradual transformation of samples, whether it is due to the leaching reaction or by readsorption processes, which we propose are at the core of the low efficiency found. Polarized microscopy analysis shows the changes in the texture of the minerals after leaching indicating oxidation and the deposition of a compound on the surface, and XPS allows for a more detailed identification of surface species. Based on the results, it is postulated that the readsorption of a lead specie on the surface of the ore is acting as a passivating layer which decreases the efficiency in the recovery of silver.

COLL 191

Characterization of the antibacterial efficiency of metal nanoparticle-infused composite materials using epi-fluorescent optical trapping

Thomas J. Beckmann, thomasjbeckmann@lewisu.edu, Dany M. Danhausen, danydanhausen@lewisu.edu, Jason J. Keleher. Dept of Chem, Lewis University, Romeoville, Illinois, United States

Current research aims to develop antibacterial surfaces that successfully prevents bacterial colonization. Integration of metal nanoparticles (MNPs) into polymeric substrates has produced antibacterial nanocomposites that exhibit improved disinfectant properties. The mechanism of cell death due to colloidal MNPs is attributed to the disruption of cell respiration and replication processes as a result of metal ions produced from bacteria-MNP oxidation reactions. Mechanisms of cell death attributed to the incorporation of MNPs into polymeric substrates are still unknown. To further investigate the mechanism of cell death on MNP-functionalized nanocomposites, this research utilizes epi-fluorescent optical trapping to investigate the antibacterial properties of colloidal MNPs deposited into biomimetic materials. Au, Ag and Cu nanoparticles as well as core-shell MNPs were deposited into cellulose matrices to produce cellulose nanocomposites (CNCs). The CNCs were tested for their ability to inhibit bacterial colonization using an epi-fluorescent optical tweezer. More specifically, the epi-fluorescent optical tweezer was used to non-covalently dock a single bacterial cell to the nanocomposite surface while monitoring the viability of the cell *in situ*. Additionally, the CNCs were tested for their ability to resist biofilm formation by using a broth culture exposure method. Initial results show that Ag-functionalized CNC show the highest level of antibacterial efficiency when compared to the Au and Cu counterparts. The antibacterial activity of the nanocomposite was directly correlated to the surface functionalization of the incorporated nanoparticles.

COLL 192

Characterizing solid electrolyte interphase-layer formation using x-ray photoelectron spectroscopy in solid-state Mg-ion batteries

Hakeem K. Henry¹, hhenry12@umd.edu, Sangbok Lee². (1) Chemistry, University of Maryland, College Park, Hyattsville, Maryland, United States (2) Chemistry Building, College Park, Maryland, United States

Magnesium-ion batteries are plagued by interface issues consisting of electrolyte incompatibility, sluggish Mg-ion reaction kinetics at the cathode, and passivation layer formation on the Mg metal anode. One possible method for remedying all of these issues simultaneously is through the development of novel solid-state battery technology. One major issue with cathodes for Mg-ion storage is the loss of active material due to electrolyte dissolution. Additionally, one of the main sources of battery thermal runaway and explosion is the danger associated with the flammable organic liquid electrolytes used in these systems. The primary advantages of using a solid electrolyte include, but are not limited to, the suppression of active material dissolution and the increased safety due to the removal of flammable liquid electrolytes. In this work we demonstrate the versatility of polyoxometalates (POMs) by employing them as both the active material within the cathode and the Mg-ion conducting solid electrolyte material in a full-cell solid-state Mg-ion battery. Considered one of the most diverse classes of inorganic molecules, POMs are polyatomic clusters of early transition metals (Mo, W or Nb) joined by oxygen atoms to form a 3D framework. Known for their unique redox activity, they also possess high ionic conductivity and multiple stable reduced and oxidized states. Combined with their innate ability to delocalize electron density throughout the entire molecule without destroying the structural integrity of the molecule; POMs are ideal electrode materials for energy storage devices. By pairing the POM active material with conductive substrates, they can function as cathodes for efficient Mg-ion storage. However, without any conductive additives, the POM molecules can potentially serve as a Mg-ion conducting solid electrolyte. The functionality of this Mg solid-state battery is derived from the reactions that occur at the interface between the POM solid electrolyte and the Mg-metal anode. Using x-ray photoelectron spectroscopy (XPS), we can characterize the chemical species that form at the anode interface as a result of POM electrolyte reduction on the Mg-metal anode surface. The composition of this solid electrolyte interphase (SEI) layer on the Mg anode surface can provide insight as to why the layer is Mg-ion conductive.

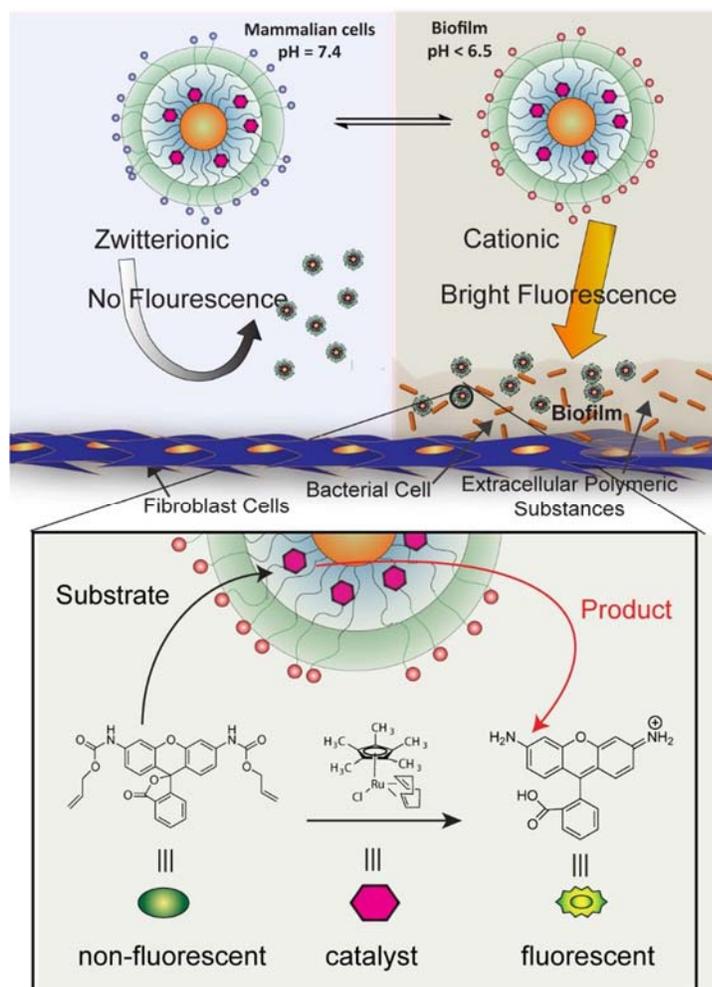
COLL 193

Charge switchable nanozymes for imaging of biofilm-associated infections

Akash Gupta¹, *akash.umass@gmail.com*, **Riddha Das**¹, **Gulen Yesilbag Tonga**¹, **Tsukasa Mizuhara**¹, **Vincent M. Rotello**². (1) *Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States* (2) *Univ of Massachusetts, Amherst, Massachusetts, United States*

Multi-drug resistant bacterial infections are responsible for 700,000 deaths each year world-wide, with more than 10 million deaths per year predicted by the year 2050. The majority of human bacterial infections (~80%) are associated with formation of biofilms on living-tissues. Early detection of biofilms is crucial for limiting infection-based damage. Imaging these biofilms is challenging: conventional imaging agents are unable to penetrate the dense matrix of the biofilm, and many are susceptible to false positive/negative responses due to phenotypical mutations of the constituent microbes. We have engineered nanomaterials to penetrate the extracellular polymeric substance

(EPS) matrix of biofilms and to intrinsically target the acidic microenvironment of the biofilms. Here, we report the creation of pH-responsive nanoparticles with embedded transition metal catalysts (nanozymes) that effectively target the acidic microenvironment of biofilms. These pH-switchable nanozymes generate imaging agents through bioorthogonal activation of profluorophores inside biofilms. The specificity of these nanozymes for imaging biofilms in complex biosystems was demonstrated using biofilm-mammalian cell co-culture experiments.



Schematic diagram showing the ability of charge-switchable nanozymes to image biofilm-associated infections.

COLL 194

Chemical and structural analysis on the surface of quantum rods

Yuetian Chen¹, *ychen208@syr.edu*, **Emily G. Ripka**², **Mathew M. Maye**¹. (1) *Department of Chemistry, Syracuse University, Syracuse, New York, United States* (2) *Chemistry, Syracuse University, Oswego, New York, United States*

Colloidal semiconductor nanocrystals such as quantum dots and quantum rods exhibit exceptional size-dependent optoelectronic properties. However, a main concern regarding the rod shape is their relatively low quantum yield comparing to spherical dots. Therefore, it's crucial for us to study the chemical composition of the ligand capping layers on QRs, which will provide insight for understanding the influence of their surface chemistry on their properties. In this presentation we will describe recent results on characterizing QRs of different aspect ratios and core/shell microstructures with transmission electron microscopy, photoluminescence spectroscopy, powder X-ray diffraction, dynamic light scattering and NMR spectroscopy. We use a combination of 1D ¹H, 2D diffusion and relaxation NMR spectroscopy to investigate the interface between the QRs and their organic capping ligands, especially the phosphonic acids. Moreover, we correlate the characterization results with the properties of the rods and propose possible approaches to develop them with more homogeneous surfaces.

COLL 195

Chemical environment of iron and nickel atoms in thin film magnets

Khuspreet Kaur¹, *kkaur45@tigermail.qcc.cuny.edu*, **Sunil Dehipawala**¹, **Pubudu Samarasekara**². (1) *Physics Dept, Queensborough Community College, Bayside, New York, United States* (2) *Physics, University of Peradeniya, Peradeniya, Sri Lanka*

Small scale magnets are in high demand due to applications in miniature electronic devices and small scale magnetic storage devices. Industry is always demanding sub-micron or even Nano-meter scale magnets. Magnetic thin films often contain several layers of coating of magnetic material. We prepared thin film magnets containing iron and nickel using spin coating and sol-gel method. The thickness of the films was controlled by the spin rate. Precursor films on the substrate were then annealed to either 200 to 350 Celcius for up to 2 hours in air. Structure of iron and nickel under various experimental conditions will be examined by X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). These tools were used to determine structural parameters such as charge state, near neighbor bond length, and number of near neighbor atoms. The results of both iron and nickel will be presented.

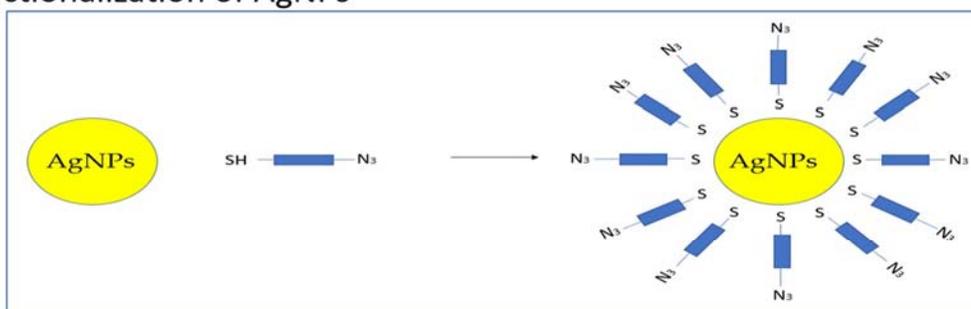
COLL 196

Click chemistry for loading a synthetic peptide (VIHW-(alkyne)-G-NH₂) onto functionalized silver nanoparticles and its antimicrobial activity against *Escherichia coli*

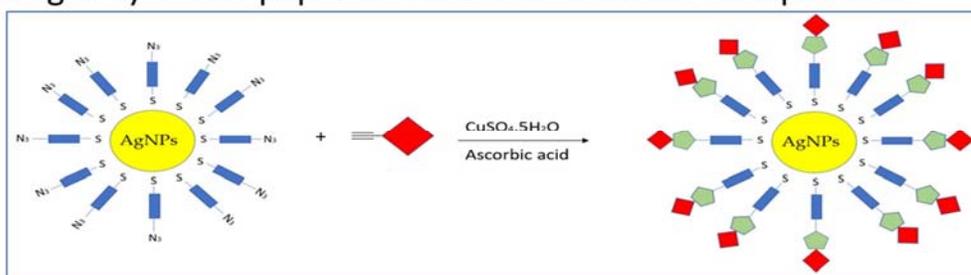
Miguel R. Gakiya¹, *mrgturya@gmail.com*, **Luis Palomino**², **Scott Pierce**³, **Alfredo M. Angeles Boza**³, **Juan C. Rodriguez-Reyes**⁴. (1) Bioengineering and Chemical Engineering, Universidad de Ingeniería y Tecnología, Lima, Barranco, Peru (2) Bioengineering and Chemical Engineering, Universidad Nacional Mayor de San Marcos, Carabayllo, Lima, Lima, Peru (3) Chemistry, University of Connecticut, Storrs, Connecticut, United States (4) Dpt. of Industrial Chemical Engineering, Universidad de Ingeniería y Tecnología, UTEC, Barranco, Lima, Peru

Infectious diseases due the bacteria with multidrug resistance are on the rise. For this reason, it is necessary to use a high concentration of antibiotics or develop novel biocides. Silver nanoparticles are efficient antimicrobials agents, which operate through various pathways and decrease the possibility of development of resistance. Antimicrobial peptides (AMPs) have been widely studied due to their broad antimicrobial spectrum, a crucial component of the host defense system. Many of the AMPs have a sequence of three amino acid starting with the amino terminal in which the third amino acid is always histidine; this sequence is known as the ATCUN motif. In the present study we loaded the synthetic peptide (VIHWG-(alkyne)-G-NH₂) into silver nanoparticles. The loading was done using click chemistry, which consisted first in the functionalization of the silver nanoparticles with SH-PEG-N₃ (MW: 1kDa) followed by the reaction with the synthetic peptide. This procedure is schematically shown in the accompanying figure. The product was characterized by UV-Vis spectroscopy, dynamic light scattering (DLS), Fourier-transform infrared spectroscopy (FTIR). Also, the antimicrobial activity of this product against *E. coli* was tested.

Functionalization of AgNPs



Loading of synthetic peptide in the functionalized nanoparticles



SH — — N₃ = SH-PEG-N₃ (MW = 1kDa)

= Synthetic peptide (VIHWG-alkyne-G-NH₂)



COLL 197

Coarse grained molecular dynamics simulations of rosette nanotubes using the MARTINI forcefield

Vyshnavi Karra, vyshi19@gmail.com, Francisco R. Hung, Hicham Fenniri. Chemical Engineering, Northeastern University, Jamaica Plain, Massachusetts, United States

Rosette nanotubes (RNTs) are biocompatible supramolecular nanostructures that are formed via self-assembly of individual, DNA-inspired guanine-cytosine (G^AC) motifs. Hydrogen bonding between the motifs lead them to assemble into rings, called rosettes. Driven by π - π interactions between the rings and hydrophobic effects, the rosettes can form RNTs where the rings are stacked or assembled into helical coils. Because of its biocompatibility, RNTs have been used in a plethora of drug delivery and biological applications, such as encapsulating dexamethasone to enhance cell growth in bones. However, a fundamental understanding of the interactions of RNTs with cell membranes, proteins and other biomolecules could lead to the development of optimal RNTs for drug delivery and other applications; for example, nanotubes tend to “stick” to the blood vessel walls at higher probabilities than spherical nanoparticles, making them more difficult to implement as drug carriers. Here we report our work in developing a coarse-grained model of these RNTs using the MARTINI forcefield. We present details of our model of the G^AC motifs, and report classical molecular dynamics simulations of individual motifs, rosettes and small RNTs in polarizable water. The purpose of these simulations is to fine-tune the interactions between the different species in our systems, as well as assess the stability of the assembled structures. Results will be compared against existing atomistic simulations and experimental data.

COLL 198

CsPbX₃ ligand binding dynamics: A 2D diffusion and relaxation NMR study

Emily G. Ripka¹, egyerdon@syr.edu, Christina R. Deschene³, Mathew M. Maye². (1) Chemistry, Syracuse University, Oswego, New York, United States (2) Department of Chemistry, Syracuse University, Syracuse, New York, United States (3) Chemistry, Syracuse University, Syracuse, New York, United States

This presentation focuses on the development of purification, halide exchange, and ligand exchange techniques for CsPbX₃ (X = Cl, Br, or I) perovskite nanoparticles (NPs) via study with 2D diffusion and relaxation ordered NMR spectroscopies. We recently demonstrated CsPbX₃ NP's ability to quantify halide ions in non-aqueous media which is facilitated by their propensity to undergo rapid halide exchange and their labile surface ligands. In this presentation we will describe recent experiments designed to study interactions at the inorganic NP core-organic ligand interface to elucidate the primary reason for this. We studied ligand binding strength and ligand surface proximity via diffusion and relaxation ordered NMR spectroscopies (DOSY and ROSY) respectively, throughout the purification, halide exchange, and ligand exchange of

CsPbBr₃ NPs. Importantly, ligand binding strength and NP surface proximity were found to decrease when successive purification and/or halide/ligand exchange steps were taken without careful concurrent additions of acid and base ligands. This suggests that ligands added during post-synthetic processing steps come to the surface of the NP, passivating open surface sites. Coupled with UV-visible (UV-vis) and fluorescence spectroscopic analyses, we will further show that this phenomenon can be utilized to replace the parent organic ligand shell with ligands of similar/differing functionality and/or chain characteristics. The techniques utilized, results, and importance for the handling of CsPbX₃ perovskite NPs will be discussed.

COLL 199

Cytosolic siRNA delivery using nanoparticle-stabilized nanocapsules for *in vivo* anti-inflammatory therapy

Yuanchang Liu¹, yuanchangliu@chem.umass.edu, Ying Jiang², Joseph Hardie³, Riddha Das⁴, Ryan Landis⁵, Vincent M. Rotello⁶. (1) Chemistry, Umass Amherst, Amherst, Massachusetts, United States (2) University of Florida, Gainesville, Florida, United States (3) University of Massachusetts Amherst, Amherst, Massachusetts, United States (4) Umass Amherst, Amherst, Massachusetts, United States (6) Univ of Massachusetts, Amherst, Massachusetts, United States

Overproduction of tumor necrosis factor- α (TNF- α) by macrophages plays a pivotal role in the development and pathogenesis of inflammatory disorders. RNA interference (RNAi) against the pro-inflammatory cytokine TNF- α offers a novel approach to precisely manipulate the immune system at a molecular and cellular level. However, therapeutic efficiency is impeded by siRNA degradation, minimal cellular delivery, and endosomal entrapment. We have recently developed nanoparticle-stabilized nanocapsules (NPSCs) for direct cytosolic siRNA delivery that facilitates siRNA translocation and avoids endosomal entrapment *in vitro* and *in vivo*. Using an LPS-induced inflammation model, we demonstrated high knockdown efficiency (~70%) of TNF- α secretion in serum by tail vein injection at a low siRNA dose of 0.28mg/kg. Therefore, this NPSCs system provides a new platform to significantly enhance the *in vivo* siRNA delivery efficiency for therapeutic applications.

COLL 200

Dense suspension rheology studies of attractive nanoemulsions for characterization of polymer chain conformation-driven dipolar interdrop association

Jin Yong Lee², ejy0206@naver.com, Minchul Sung², Kyounghee Shin², Ji Eun Kim², Sung Jun Hong², Jin Woong Kim^{1,2}. (1) Chemical and Molecular Engineering, Hanyang University, Ansan, Korea (the Republic of) (2) Bionano technology, Hanyang University, Ansan, Korea (the Republic of)

This study introduces an attractive nanoemulsion (ANE) system that is characterized by the reversible dipolar interaction between drops induced by hydrophilic polymer chain conformation on their surface. For this, we first synthesized amphiphilic ABA triblock copolymers, poly (ethylene oxide)-*b*-poly (ϵ -caprolactone)-*b*-poly (ethylene oxide) (PEO-*b*-PCL-*b*-PEO) via urethane condensation reaction, while controlling their molecular weights and block ratios. When the triblock copolymer is associated with lecithin, the interdroplet attractions over a wide volume fraction range of the dispersed oil phase occurred. Thanks to formation of a percolated network of stable drops, our ANEs exhibited the outstanding emulsion stability without any changes in the drop size, even in a highly-concentrated state (close to 0.7 fraction) and in the repeated freeze-thaw test. From the dense suspension rheology studies, interestingly, we figured out that the enhanced modulus of ANEs at room temperature was attributed to the effective association of PEO chains with lecithin occurring across droplets. Furthermore, we observed that the longer the molecular weight of PEO, the more easily interdrop association occurred. This implies that the chain conformation of the PEO plays an important role in regulation of the droplet-droplet association of ANEs. All these findings support the potential use of our ANE system over a wide range of applications in drug delivery, cosmetic and food formulations, and life sciences.

COLL 201

Dermal-epidermal junction-targeted transdermal delivery using squashy, skin-adhesive polymeric nanovehicles

Sung Jun Hong¹, tjdwms6015@gmail.com, **Jae Sung Park**², **Ji Eun Kim**¹, **Jin Yong Lee**¹, **Ho Lee**^{2,4}, **Jin Woong Kim**^{1,3}. (1) Bionano Technology, Hanyang University, Ansan, Korea (the Republic of) (2) Mechanical Engineering, Kyungpook National University, Daegu, Korea (the Republic of) (3) Chemical and Molecular Engineering, Hanyang University, Ansan, Korea (the Republic of) (4) Laser Application Center, Kyungpook National University, Daegu, Korea (the Republic of)

Dermal-epidermal junction (DEJ) is the basement membrane made of specialized extracellular matrix containing a few collagens and specific proteins. Since DEJ has a large number of skin cells around it, it plays a very important role in promoting skin physiological activity. If a skin active can be delivered intensively to DEJ, it is expected that the skin physiological activity would be further enhanced. Recently, nanoscale colloidal particles such as micelles, liposomes, and polymeric and inorganic particles have been widely studied as carriers for transdermal delivery. In particular, polymeric nanoparticles have a great potential in delivering the active through the skin, thanks to their advantageous characteristics such as non-toxicity, long-term stability, and permeation efficacy for drugs. This study introduces a new transdermal delivery system in which polymeric nanovehicles can deliver intensively the skin active to DEJ. For this, we fabricated phase modulus-regulated polymeric nanovehicles through co-assembly of amphiphilic triblock copolymers, poly (ethylene oxide)-*b*-poly (ϵ -caprolactone)-*b*-poly (ethylene oxide) and poly (ethylene oxide)-*b*-poly (propylene oxide)-*b*-poly (ethylene oxide). The modulus of micelle core phase could be tuned by changing the composition

of the two triblock copolymers. We showed that control over the softness of the polymeric nanovehicles was essential for enhancing the delivery efficiency of the skin active to DEJ, as it determined the diffusivity of the active through the skin. We also figured out that conjugation of cell-penetrating peptide (CPP) to the squashy polymeric nanovehicles further enhanced drug delivery to the DEJ layer. These results demonstrated that squashy, skin-adhesive polymeric nanovehicles were very useful for DEJ-targeted transdermal delivery.

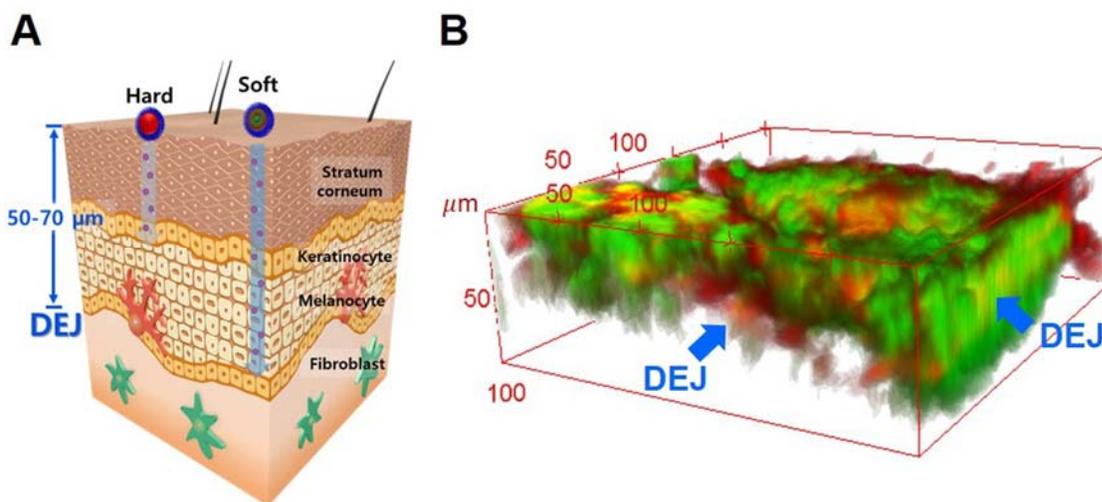


Figure 1. (A) Schematic illustration for DEJ-targeted transdermal delivery using squashy polymeric nanovehicles. (B) 3-D profile of skin depth-penetration of model fluorescence probes that are loaded in polymeric nanovehicles.

COLL 202

Design of nickel nanoparticles for X-ray fluorescence microscopy to visualize cellular metal ion concentrations

Hamzah Sawab, hsawab@pdx.edu, **Marilyn R. Mackiewicz**, mackiewi@pdx.edu. Chemistry, Portland State University, Beaverton, Oregon, United States

Copper metal ion homeostasis is tightly regulated in cells for biological activity and is proposed to be localized in copper storage pools that can be readily available depending on a need intra- and extracellularly. There is a critical need for identifying the location of these copper storage pools in subcellular compartments as it will help us to identify the role of copper in biological processes and diseases. This has been challenging as methods for detecting subcellular localization of metal ions does not exist. Unlike proteins, most metals cannot be readily detected by routine biochemical assays. Consequently, there is a gap in knowledge regarding cellular and intracellular distribution of important biological metals involved in many different cellular pathways. While there are fluorescent sensors that can detect labile metal ions such as copper

(rhodamine dye) and iron (Perl's stain), these assays require high local concentrations of metal ions to be effective. Most recently, X-ray fluorescence microscopy (XFM) has emerged as a powerful tool to visualize metals within cells or tissue to produce elemental maps of metal ion localization in cellular and subcellular regions such as the mitochondria. While fluorescent dyes are able to label subcellular organelles, there is no strategy to correlate elemental concentration and distribution with distinct subcellular compartments. There is a great need to bridge the synergy of XFM with nanoparticle-based probes that are specific for subcellular organelles. Here we will discuss the design and synthesis of hybrid lipid-coated nickel nanoparticles as nanoprobe for site-directed targeting of subcellular organelles such as the mitochondria, nucleus, Golgi, endoplasmic reticulum, and lysosomes. Dynamic light scattering and UV-Vis spectroscopies will be used to show that these nanoprobe to be stable under physiological conditions with minimal surface oxidation and release of nickel ions that lead to instability. With these nanoprobe we will be able to correlate and map elemental concentration and localization with distinctive subcellular organelles that play important roles in diseases involving metal ion homeostasis such as Alzheimer's and Wilson's disease.

COLL 203

Determination of permethrin level on military uniform fabrics using desorption-gas chromatography–mass spectrometry

Judith B. Sennett¹, judith.b.sennett.civ@mail.mil, Rose A. Pesce-Rodriguez², Andres A. Bujanda², Lauren B. Blaudeau³. (1) U.S. Army Natick Soldier RDEC, Natick, Massachusetts, United States (2) U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States (3) Oberlin College, Oberlin, Ohio, United States

Military uniform materials are treated with permethrin in order to provide protection to the soldier from mosquito and tick bites, thus preventing insect borne diseases such as malaria, Lyme disease, dengue fever, and others. However, the durability of the permethrin treatment is variable, and has been shown to be subject to loss from laundering and wear, especially in harsh conditions. It is important to be able to monitor the amount of permethrin on the fabric, both initially, and after field use and laundering. To do this, laboratory methods have been established to quantify the amount of repellent on the fabric surface, and to follow the loss of repellent as a result of multiple laundering cycles. However, the current analytical method is cumbersome, relying on solvent extraction of fabric specimens and subsequent analysis by gas chromatography mass spectrometry (GC-MS).

A new method using desorption-gas chromatography–mass spectrometry (D-GC-MS) as a screening tool for quantifying the surface concentration of permethrin on military fabrics has been developed. This allows for the direct analysis of fibers without the use of solvent extraction, making the new method both quicker and greener as compared with current practice. Sample sizes are minimal; the method utilizes 1-2 mg of fabric which are cut from the fabric piece, or are fibers extracted from a cut edge. Since little

material is required for D-GC-MS analysis, it is also possible to analyze fibers pulled from different areas of the fabric and use the results to determine uniformity of the permethrin finish.

The method was demonstrated for permethrin only, however, it is expected to be applicable to other treatments as well.

COLL 204

Developing the sapphire (0001) surface as a transparent substitute for mica for DNA nanostructure imaging

Michael L. Norton, norton@marshall.edu, Masudur Rahman, David Neff, Zachary T. Boggs. Chemistry, Marshall University, Huntington, West Virginia, United States

Mica has been used almost exclusively by the DNA nanostructures community because it is an atomically flat and non-perturbative substrate with exceptionally tunable DNA adhesion properties. Other “van der Waals” layered materials, including graphite, h-BN and MoS₂, which also demonstrate excellent cleavage properties have been evaluated as potential atomically flat substrates, optimal for imaging ultrathin DNA based structures. These layered materials have been found to significantly re-organize the programmed structures of origami constructs. While far from a comprehensive survey, these results suggest that the same van der Waals forces stabilizing most two dimensional materials are able to compete well with the van der Waals forces stabilizing DNA nanostructures. Al₂O₃, a 3D ionic material with high chemical, mechanical and thermal stability has been evaluated as an alternative substrate. Additional properties recommending sapphire include its transparency and the fact that crystal growth is already at a high level of technological development.

The surfaces of sapphire “window” samples, ranging from the “as received” form to samples annealed under dry and wet conditions have been characterized using AFM. Increasing annealing temperature leads to a reduction in the corrugation attributable to scratches and gouges. Terraces become apparent after high temperature annealing. A representative AFM image of cross shaped DNA origami structures on a high temperature annealed sapphire surface is provided in Figure 1. Relatively high surface populations of undistorted origami are readily discernable. Under similar origami dosing conditions, mica surfaces display similar coverage. Many anticipated origami surface modifications will therefore remain visible when this substrate is used as a technologically accessible alternative to the mica surface.

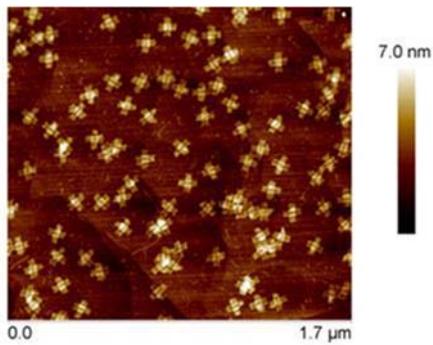


Figure 1 AFM image of origami constructs on sapphire window annealed at 1200 °C

COLL 205

Development of nucleic acid delivery system targeting Ras gene by β -glucan

Shogo Sasaki¹, 12shogo05@gmail.com, **Nobuaki Fujiwara**¹, **Hiroto Izumi**², **Kazuo Sakurai**³, **Shinichi Mochizuki**⁴. (1) Chemistry and Biochemistry, The University of Kitakyushu, Kitakyushu, Japan (2) University of Occupational and Environmental Health Japan, Kitakyushu, Japan (3) U of Kitakyushu Dept of Chem, Kitakyushu Fukuoka, Japan (4) The University of Kitakyushu, Fukuoka, Japan

Introduction

Therapeutic oligonucleotide such as antisense-oligonucleotide (AS-ODNs) has been paid great attention because it can specifically hybridize with mRNAs, resulting in interference with the splicing mechanism or the regulation of protein translation.

Therefore, the reduction of side effects is expected.

Rat Sarcoma (Ras) gene is a kind of major oncogene. There are three isoforms K-Ras, N-Ras and H-Ras. K-Ras mutation is frequently observed in cancer cells. In normal cells, Ras protein forms active type and inactive type. The active type Ras induces cell proliferation by binding the small molecule GTP. However, in cancer cells having the gene mutations with multiple patterns, Ras always activates, resulting in continuing to send the cell proliferation signal.

We have reported that Schizophyllan (SPG) is complexed with ODN and this complex is recognized by β -glucan receptor Dectin-1, β -glucan receptor. Dectin-1 is known to express on immune cells such as macrophage and dendritic cell, and some cancer cells such as lung cancer.

In this study we demonstrated the exploration of the optimal AS-ODN sequence for K-Ras and evaluated the gene expression efficiency by the complex.

Method

We prepared 78 antisense ODNs for K-RAS (K-AS-ODN). After the transfection to Panc 1 cells, human pancreatic epithelioid carcinoma, we evaluated the cell viability by WST-8 assay. After treatment with K-AS-ODN, the expression level of K-Ras protein was confirmed by Western Blotting. We added SPG/K-AS-ODN complex to Panc1 cells and evaluated the cell viability.

Result and Discussion

Among 78 K-AS-ODNs, 5 AS-ODNs showed a strong inhibition efficiency for Panc-1 cell growth. Considering a secondary structure of K-Ras mRNA obtained by CentroidFold, the five sequences can be easy to bind to a single chain region. The addition of SPG/K-AS-ODN to the cells suppressed not only the gene expression but the cell proliferation. These results could facilitate the clinical application of the complex for cancer therapy.

COLL 206

Development of tumor-specific double-stranded RNA delivery system using hyaluronic acid

*Masashi Umeda*¹, z8mab004@kitakyu-u.ac.jp, *Shinichi Mochizuki*². (1) chemistry and biochemistry, The University of Kitakyushu, Kitakyushu, Japan (2) The University of Kitakyushu, Fukuoka, Japan

Introduction

Cytotoxic T cells (CTL) attack cancer cells by recognizing cancer-specific antigens presented on the cellular surface. However, some cancer cells suppress the expression of MHC-class I to escape from such an immune system. It is known that double-stranded RNA (dsRNA) recognized by Toll-like receptor 3 (TLR3), inducing interferon response. This results in the induction of MHC-class I expression. Therefore it is expected to express MHC-class I molecule again by delivering dsRNA to cancer cells specifically.

However, nucleic acids are easily degraded by enzymes and rapidly excluded via kidney after injection. We have studied hyaluronic acid (HA) as delivery carrier to cancer cells. HA is a linear polymer consisting of glucuronic acid and N-acetylglucosamine. Because cancer cells express CD44, a one of major HA receptor, on cellular surface, we think that HA-modified dsRNA can be efficiently delivered to cancer cell through CD44.

Method

As a model of the conjugation between HA and dsRNA, we prepared single chain oligo nucleotides modified with an amino group at the 5'-terminal to make a conjugate with carboxyl group of HA. We used 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) as crosslinking agents. EDC and NHS, DMSO solution were added to HA (1.0 in 10 mM MES solution and incubated for 2 hours. After that, oligo nucleotide solution added and incubated overnight. The molar ratio in the reaction mixture was HA : oligo nucleotide = 1 : 25 (HA/ON 25) and 1: 50 (HA/ON 50).

Results

The conjugation was evaluated with gel permeation chromatography. When we determined the reaction yields from the peak areas between free oligo nucleotide and reaction mixture by UV measurement (260 nm), HA/ON25 and HA/ON50 were 20% and

6%, respectively. This difference in the reaction efficiency is considered to be attributed to the water content in the reaction mixture because the activated ester of HA-NHS is soon hydrolyzed in water.

COLL 207

Diatom-inspired silica nanoparticle coatings using an engineered mussel glue to accelerate bone growth on titanium-based implants

*Yun Kee Jo², Bong-Hyuk Choi², **Chang Sup Kim¹**, cskim1409@ynu.ac.kr, Hyung J. Cha³. (1) Chemistry and Biochemistry, Yeungnam University, Pohang, Korea (the Republic of) (2) POSTECH, Pohang Kyungbuk, Korea (the Republic of) (3) Chem Eng, Pohang University Sci and Tech, Pohang Gyeongbuk, Korea (the Republic of)*

Silica nanoparticles (SiNPs) have been utilized to construct bioactive nanostructures comprising surface topographic features and bioactivity that enhance the activity of bone cells onto titanium-based implants. However, there have been no previous attempts to create microrough surfaces based on SiNP nanostructures even though microroughness is established as a characteristic that provides beneficial effects in improving the biomechanical interlocking of titanium implants. Herein, we propose a protein-based SiNP coating as an osteopromotive surface functionalization approach to create microroughness on titanium implant surfaces. A bioengineered recombinant mussel adhesive protein fused with a silica-precipitating R5 peptide (R5-MAP) enables to directly control the microroughness of the surface through the multilayer assembly of SiNP nanostructures under mild conditions. The assembled SiNP nanostructure significantly enhances the in vitro osteogenic cellular behaviors of preosteoblasts in a roughness-dependent manner and promotes the in vivo bone tissue formation on a titanium implant within a calvarial defect site. Thus, the R5-MAP-based SiNP nanostructure assembly could be practically applied to accelerate bone tissue growth to improve the stability and prolong the lifetime of medical implantable devices.

COLL 208

Direct cytosolic co-delivery of siRNA and tamoxifen for enhanced breast cancer therapy

***Joseph Hardie¹**, jhardie7@gmail.com, Ying Jiang¹, Emily Tetrault², Phaedra Ghazi¹, Gulen Yesilbag Tonga¹, Michelle E. Farkas³, Vincent M. Rotello⁴. (1) University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Mount Holyoke College, South Hadley, Massachusetts, United States (3) Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States (4) Univ of Massachusetts, Amherst, Massachusetts, United States*

Using siRNA-mediated protein knockdown with small molecule drugs to target multiple cell signalling pathways can result in more effective combination cancer therapies. In this work, nanoparticle-stabilized capsules (NPSCs) consisting of a linoleic acid oil core,

surface coated with positively charged arginine functionalized gold nanoparticles, are used to co-deliver survivin-targeted siRNA and tamoxifen for breast cancer therapy. The NPSC hydrophobic core allows the vehicle to enter cells through a non-endocytotic lipid-based mechanism, causing direct delivery of encapsulated cargo to the cytosol. This delivery strategy contrasts traditional delivery vehicles that rely on endocytosis, resulting in endosomal entrapment, and reduces the effective concentration of delivered cargo that acts on the cell. Non-endocytotic cargo delivery maximizes the potency of the agent by allowing internalized molecules to interface directly with the cellular components needed to produce the intended biological effect. The modular nature of the NPSC vehicle allows for orthogonal loading of negatively charged biologics and hydrophobic molecules, allowing simultaneous delivery of chemically distinct combinations. The advantage of this co-delivery was demonstrated through NPSC co-delivery of tamoxifen and survivin-targeted siRNA into breast cancer cells, inducing apoptosis by disabling pro-tumorigenic pathways and resulting in enhanced breast cancer cell killing.

COLL 209

Direct, *in situ* visualization of graphene reaction dynamics via optical microscopy

Wan Li, wl285@berkeley.edu, Michal Wojcik, Yunqi Li, Ke Xu. Department of Chemistry, University of California, Berkeley, Berkeley, California, United States

The utility of rising two-dimensional (2D) materials, such as graphene, can be substantially expanded through chemical reactions and functionalizations. However, it has been a challenge to probe the key parameters controlling such processes. We recently developed a facile optical microscopy approach, interference reflection microscopy (IRM), to quantitatively reveal the redox reaction dynamics of graphene and graphene oxide (GO) *in situ* with ~300 nm spatial resolution and video-rate (25 frames/second) temporal resolution. In this presentation, we first show how such capabilities enable us to reveal the surprising oxidation kinetics of graphene, which is characterized by a seeded, autocatalytic process that gives rise to unique, wave-like propagation of reaction in 2D at the nanoscale. By integrating our optical detection scheme with electrochemistry, we next demonstrate the possibility to achieve reversible, rapid oxidation and reduction of graphene, and reveal that the electrochemical oxidation of graphene is characterized by rich spatiotemporal dynamics controlled by applied voltage, intrinsic and reaction-induced local defects, as well as reaction-induced change in electrical conductivity. While the ability to reveal these striking, spatially resolved reaction dynamics *in situ* is already fascinating, our work also opens the door to future, mechanistic studies of other chemical reactions of 2D materials.

COLL 210

Dynamic double emulsions generated via *in situ* surfactant synthesis

Cassandra A. Zentner, *cassandra.zentner@gmail.com*, Timothy M. Swager. Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

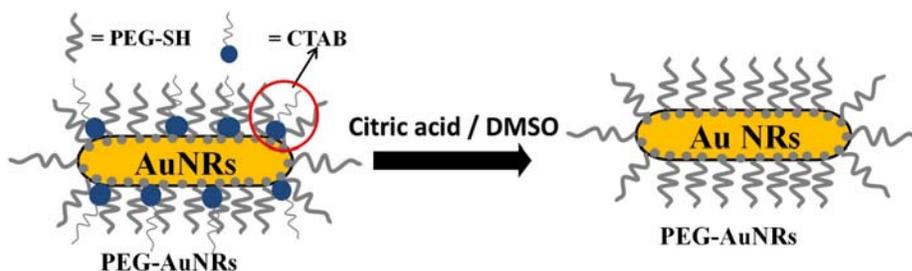
Dynamic double emulsions are powerful sensing materials for aqueous applications, translating chemical responses to observable morphological changes. Engineering surfactants to respond to analytes can involve extensive post-functionalization after emulsification. Post-functionalization is time intensive and the extent of functionalization is difficult to characterize. In this presentation, we report the use of click chemistry to generate surfactants *in situ*. Via this method, both the surfactants and double emulsions are produced instantaneously, bypassing post-functionalization. Initial efforts focused on imine generation, by the interfacial reaction between amine functionalized reagents in continuous aqueous phase and aldehydes in one of the organic phases. During emulsification, the imine surfactant was synthesized *in situ* in under 10 seconds, yielding stable double emulsions. Our results provide a step towards efficiently synthesizing complex surfactants for the use in sensing applications.

COLL 211

Effective removal of surface-bound cetyltrimethylammonium ions from PEG-protected Au nanorods by treatment with dimethyl sulfoxide/citric acid

Hideya Kawasaki¹, *hkawa@kansai-u.ac.jp*, **Ryuichi Arakawa**². (1) Kansai University, Osaka, Japan (2) Fac. of Chem. Materials and Bioeng., Kansai University, Suita, Japan

Cetyltrimethylammonium bromide (CTAB)-based surfactants are typically used as morphology-directing/stabilising agents for gold nanorods (AuNRs), forming bilayers on their surface. However, the biological applications of AuNRs require the removal of surface-bound CTAB due its high toxicity and the poor colloidal stability of CTAB-covered AuNRs in biological media. Herein, we report a simple and effective strategy for removing surface-bound cetyltrimethylammonium (CTA) cations from poly(ethylene glycol) thiolate-protected AuNRs (PEG-AuNRs) by treatment with dimethyl sulfoxide/citric acid (DMSO/Cit), achieving residual CTA ion levels that cannot be unambiguously detected by highly sensitive mass spectrometry or X-ray photoelectron spectroscopy (XPS) techniques. The DMSO/Cit treatment is thought to destabilise the Ag-Br-CTA complex on AuNRs, since citric acid forms strongly bound chelate complexes with CTA cations.



COLL 212

Effects of ALD layers on magnesium anode interface chemistry

Emily Sahadeo¹, esahadeo@umd.edu, **Chuan-Fu Lin**^{2,3}, **Gary Rubloff**^{2,3}, **Sangbok Lee**¹. (1) Chemistry, University of Maryland, College Park, Maryland, United States (2) Materials Science and Engineering, University of Maryland, College Park, Maryland, United States (3) Institute for Systems Research, University of Maryland, College Park, Maryland, United States

Magnesium (Mg) batteries have sparked interest as an alternative energy storage technology to Lithium ion (Li-ion) batteries due to magnesium's abundance, increased volumetric capacity over Li and graphite anodes, and fewer safety hazards associated with Mg-based systems. Considering the electrode surfaces and interfaces, the transport of ions is crucial to battery performance. Regarding anodes, in Li-ion batteries the solid electrolyte interphase (SEI) which forms at the anode/electrolyte interface allows Li ion movement and does not hinder electrochemistry. Conversely, in Mg batteries using many conventional electrolytes the SEI layer that forms on Mg is a blocking layer through which Mg ions cannot easily diffuse. Due to this problem, Mg battery research has largely focused on developing new electrolytes to circumvent the issue of a passivation layer on Mg anodes, however these are often time-consuming and costly to make.

We propose that investigating the anode surface at the electrode/electrolyte interface is necessary to gain better understanding of what specific processes and reactions are occurring and how they impact chemistry at the electrode boundaries, with a goal of implementing simpler electrolytes. Artificial SEI layers have been demonstrated to help minimize unwanted reactions at Li electrode surfaces, so we are interested in how artificial SEI layers can help improve understanding of Mg surface chemistry. In this work, a study of interfacial chemical reactions at the Mg anode is presented. Specifically, Atomic Layer Deposition (ALD) is used to apply precisely controlled layers to the surface of the Mg anode and investigate whether these pre-applied films can help protect Mg from passivation by the electrolyte and improve Mg deposition and stripping at the interface. Electrochemical data will be presented with XPS and SEM-EDS analyses to demonstrate how nanometer-thin ALD layers affect Mg anode electrochemistry, with the aim to improve Mg anode performance and utilize non-complex electrolytes.

COLL 213

Effects of antifreeze proteins and their hyperactive mutants on calcite crystallization

Audrey Kishishita², akishis@calstatela.edu, **Joshua J. Lugo**², Joshlugo@hotmail.com, **Fabio Rojas**¹, rojas.fabio24@gmail.com, **Jose O. Castellon**^{2,3}, joseomar805@gmail.com, **Xin Wen**², xwen3@calstatela.edu. (1) Biology,

California State University, Los Angeles, Los Angeles, California, United States (2) Chemistry & Biochemistry , California State University Los Angeles, Los Angeles, California, United States (3) Biological Sciences, University of California, Los Angeles, Los Angeles, California, United States

Formation of inorganic salts (i.e., scale deposits) is a problem in industrial and domestic setting. To control scale deposits, chemical scale inhibitors are commonly used. Commercial antiscaling agents include polyelectrolytes that dissociate potentially harmful phosphonates, carboxylates, and sulfonates anionic groups. Thus, it is imperative to identify highly efficient polymeric inhibitors to replace phosphonate inhibitors due to their environmental risks. Ice-binding proteins or antifreeze proteins (AFPs) from cold-adapted organisms can bind to specific ice surfaces, thereby inhibiting the nucleation and crystallization of ice. AFPs can also control the crystallization of some non-ice like compounds by interacting with the crystalline surfaces of these compounds. We correlate the charge and molecular properties of the polyelectrolytes with their efficiencies in inhibiting the scale crystal formation. A beetle AFP from *Tenebrio molitor* (TmAFP) having regular spaced charged residues on its surfaces is prepared and studied here. Calcium carbonate (CaCO_3) is a scalent of interest in this study. We investigate the effects of TmAFP and their mutants on the formation of CaCO_3 . One TmAFP mutant (D4) was modified with aspartate residues interspersed at equidistance apart from each other. The second TmAFP mutant (N5) was modified by removing all negatively charged residues, aspartate and glutamate, and replacing them with asparagine. Results show that the presence of TmAFP inhibits the formation of CaCO_3 , resulting much fewer CaCO_3 crystals. The effect is more pronounced in the mutants. By analyzing the charged residues on the surfaces of TmAFP and calcite surfaces, we propose that TmAFP may affect the formation of calcite via adsorption to the crystalline surfaces of CaCO_3 . This study provides better understanding for scale control as well as new designs for green antiscalants.

COLL 214

Encapsulation of plasmid DNA by cationic nanocarriers for cellular uptake by microspores

Jae-Young Cho¹, Pankaj Bhowmik¹, Sabine Dodard¹, Patricia Polowick¹, Goska Nowak¹, Hicham Fenniri², Usha Hemraz¹, usha.hemraz@nrc-cnrc.gc.ca. (1) National Research Council of Canada, Montreal, Quebec, Canada (2) Chemical Engineering, Northeastern University, Boston, Massachusetts, United States

The delivery of nucleic acids into cells allows manipulation of genes, which can be useful in suppressing disease or undesired genes. However, cellular delivery of such materials, namely, DNA, RNA, proteins and other macromolecules is a challenge due to repulsive electrostatic forces. Encapsulation of negatively charged biomolecules by cationic nanocarriers can be an interesting alternative to methods such as electroporation, gene gun and direct injection. In this work, various nanocarriers, namely rosette nanotubes (biocompatible nanomaterials generated from the self-assembly of a

bio-inspired bicycle, featuring the hydrogen bonding arrays of guanine and cytosine), peptides with tunable properties such as size, charge and functional groups, and polysaccharide-based materials were synthesized and characterized by microscopy, dynamic light scattering and zeta potential measurements. Some of these cationic nanomaterials were found to bind with plasmid DNA via electrostatic interactions at physiological conditions. The resulting complexes were successfully and reproducibly internalized by developing microspores, as evidenced by fluorescence. Various protocols for the release of DNA from the complexes were also explored.

COLL 215

Engineered antibacterial nanosurfaces for field hospitals

James W. Moxley¹, moxley.j@husky.neu.edu, **Thomas Webster**². (1) *Chemical Engineering Department , Northeastern University, Boston, Massachusetts, United States* (2) *Chemical Engineering Department , Northeastern University , Boston, Massachusetts, United States*

Almost two decades following the turn of the twenty-first century, antibiotic resistant bacteria continue to demonstrate an ever escalating threat within even the most advanced health care networks of the developed world. In addition to this ongoing situation, many developing nations are still afflicted with persistently high disability and mortality rates which stem from bacterial strains that have not acquired resistance, and could thus be readily treatable if an effective system for antibiotic distribution and implementation were established. With limitations ranging from resistant phenotype generation amongst pathogenic targets, to thermal stability concerns over distant transit, conventional small-molecule antibiotics face numerous shortcomings in addressing challenges with clinically acquired bacterial infections. As a new approach towards the development of consistent and reproducible aseptic surfaces, selenium nanoparticulate coatings were nucleated on numerous solid supports that are commonly employed for the construction of field hospitals. In order to mimic the diverse environments in which these stations operate, the coated surfaces were subjected to variant heating conditions and set into culture within gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) bacterial strains. Bacterial localization and growth on these surfaces was initially surveyed by means of Colony Forming Unit (CFU) assay at set time scales following initial exposure. Although selenium-based nanocoatings have demonstrated a statistically significant reduction in gram positive bacteria colonization on treated surfaces, responses from gram negative bacteria are varied within an overall trend of reduction. Ongoing studies in this project are focused on determining the separate effects of geometry and chemistry along nanorough surfaces, specifically to elucidate the mechanism by which antibacterial properties are achieved, such that next-generation, nanopatterned surfaces may be developed and optimized for clinical application. Studies on bacterial phenotypic response to nanoparticulate functionalized surfaces, specifically expression pathways towards biofilm production and maintenance, will also be investigated within this work.

COLL 216

Engineering immune cell-derived hybrid exosomes for tumor-targeted drug delivery

Sagar Rayamajhi^{1,2}, srayamajhi@ksu.edu, Tuyen Nguyen^{1,2}, Achini Eliyapura^{1,2}, Ramesh Marasni^{1,2}, Santosh Aryal^{1,2}. (1) Chemistry, Kansas State University, Manhattan, Kansas, United States (2) Nanotechnology Innovation Center of Kansas State (NICKS), Kansas State University, Manhattan, Kansas, United States

Exosomes are natural nanocarriers that play a significant role in intercellular communication and signaling processes. Depending on the type of parent cells, the secreted exosomes display distinctive biological function with the preservation of naïve properties of the parent cell. Towards this direction, we hypothesize that the immune cell-derived exosomes will preserve inherent immunogenic properties which can be further used for therapeutic application, for example, targeted drug delivery. However, the series of ultra-centrifuge based exosomes isolation result in lower yield limits its application, which is the major roadblock to implement exosomes in drug delivery. Herein, our overarching hypothesis is that by hybridizing exosomes with a synthetic liposome, a solution in drug delivery can be achieved by increasing the number of the hybrid exosome. Along this line, we re-engineered exosomes by integrating mouse macrophage (J774A.1) derived immuno exosomes with synthetic liposome following extrusion method. Formation of hybrid exosomes was monitored and confirmed by fluorescent resonance energy transfer (FRET), which showed diminished FRET effect due to the increased distance between two FRET pairs in hybrid exosomes. Furthermore, SDS-PAGE electrophoresis confirmed the successful translocation of surface protein markers from exosomes into the hybrid exosomes. An in vitro specificity of hybrid exosomes was studied with a mouse breast cancer cell (4T1) and human breast cancer cells MDA-MB-231 and MCF-7. Normal human breast (MCF-10A) and normal mouse fibroblast (NIH-3T3) cells were used as a normal control to evaluate the cancer cell specificity of the hybrid exosomes. Cellular internalization of hybrid exosomes was studied using flow cytometry and confocal imaging, which showed higher accumulation in cancer cell than that of normal cells. Moreover, the hybrid exosomes showed biocompatibility when tested with normal cells with more than 85% cellular viability. These results suggest that the engineered hybrid exosomes could be an exciting platform technology for tumor-targeted drug delivery.

COLL 217

Engineering the magnetic permeability in magnetic nanoparticles using dendritic ligands

Jennifer D. Lee¹, jleed@sas.upenn.edu, Davit Jishkariani^{1,7}, Hongseok Yun¹, Taejong Paik², James M. Kikkawa³, Cherie R. Kagan^{4,1}, Bertrand Donnio^{5,7}, Christopher B. Murray^{2,6}. (1) Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States (3) Physics and Astronomy, University of Pennsylvania, Philadelphia,

Pennsylvania, United States (4) Dept of ESE MSE, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States (5) CNRS–Université de Strasbourg, STRASBOURG, France (6) Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States (7) Complex Assemblies of Soft Matter Laboratory (COMPASS), CNRS-Solvay-University of Pennsylvania, Bristol, Pennsylvania, United States

The collective magnetic properties of nanoparticles (NPs) are greatly affected by the nature of neighboring particles and the inter-particle interactions. The increase in dipole-dipole interactions can increase the ferromagnetic resonance (FMR) frequencies, which often limits the operable frequency ranges of AC magnetic devices. In this contribution, a series of dendritic ligands with various end-groups have been designed to bind colloidal magnetic NPs *via* ligand exchange. The design of dendrons is based on 2,2-bis(hydroxymethyl)propionic acid scaffold with one end for binding NPs and the other end with several fatty acid segments. The inter-particle spacings controlled by generations of dendrons fall between the range of commercial ligands and DNA-based ligands. The decrease in dipole-dipole interactions driven by increasing inter-particle spacing was determined by the direct current and alternating current magnetic properties of magnetic NPs. Particularly, the increase in FMR frequency of the manganese zinc ferrite NPs suggests the potential of this approach to increase the FMR limit to higher frequency ranges. The dendritic effect and the correlation between dipole-dipole interactions and magnetic properties of magnetic NPs will be discussed.

COLL 218

Engineering the titania nanostructure to optimize visible light-driven antimicrobial properties

Sameera Wickramasinghe¹, smw151@case.edu, **Zhuoying Jiang**², **Xiong Yu**², **Anna C. Samia**¹. (1) Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (2) Department of Civil Engineering, Case Western Reserve University, Cleveland, Ohio, United States

Highly photoactive titania nanoparticles (TiO₂ NPs) have attracted great interest due to their potential use in many different applications. However, the large intrinsic band gap of TiO₂ (3.2 eV) remains a major obstacle that prevents its use in more practical visible light-activated photocatalytic applications. Among the strategies adapted to overcome this limitation, the introduction of non-metal dopants (N and C, respectively called N-TiO₂ and C-TiO₂) to the TiO₂ nanostructure enables the narrowing of the band gap to facilitate activation with visible light. In our study, we have investigated the photoactivity of non-metal doped TiO₂ NPs and the reactive oxygen species (ROS) generation by N-TiO₂ and C-TiO₂ nanoparticles for potential antimicrobial applications. Even though the photocatalytic activity of N-doped and C-doped TiO₂ NPs have already been heavily studied, a systematic investigation of the materials' ROS generation capability with changes in synthetic approaches has not yet been well explored. In our study, we investigated the effect of the synthetic conditions on the NP structure of N- and C-doped

TiO₂ and its corresponding influence on the ROS generation for visible light-driven antimicrobial applications.

COLL 219

Enhanced charge separation in nitrogen-doped graphene quantum dots/graphitic C₃N₄ lateral heterostructures for photocatalytic H₂ evolution

Kevin Yu, kevin.yu@mail.utoronto.ca, M. Cynthia Goh. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Photogenerated charge separation is critical for photocatalytic applications of graphitic carbon nitride (g-C₃N₄). Graphene carbon dots deposited on g-C₃N₄ are known to promote photogenerated charge separation at the interface by building heterojunctions. For more effective and fast charge carrier transfer, it is necessary to induce a lateral driving force to delocalize photocarriers around the photoexcited sites. We fabricated a novel lateral composite by growing g-C₃N₄ around nitrogen-doped graphene quantum dots (NGQD) through C-N bonds on a tertiary N. Strong electronic coupling between NGQDs and g-C₃N₄ generates new bands localized at the interface to form an electronic gradient driving charges moving laterally along the π -p- π network and extending the photosensitive region beyond 560nm. The photocatalytic H₂ evolution rate under visible light ($\lambda > 420$ nm) irradiation with NGQD/g-C₃N₄ was found to be over 8 times that of pure g-C₃N₄.

COLL 220

Enzyme-polymer-cellulose colloids: Enzymes interlocked in the fibrous matrix of cellulose with enhanced stability while preserving activities

Caterina Riccardi¹, caterina.riccardi@uconn.edu, Challa V. Kumar², Rajeswari Kasi³. (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Univ of Connecticut, Storrs Mansfield, Connecticut, United States (3) University of Connecticut, Storrs Mansfield, Connecticut, United States

The colloidal particles consisting of enzymes embedded in cellulose nanoparticles are promising for drug delivery, biocatalysis and for theoretical studies. Toward this goal, we have developed a systematic approach for the stabilization of enzymes in paper by a simple method. In our design, bovine serum albumin is used to passivate cellulose surface (BSA-Paper) while at the same time providing attachment groups for subsequent chemical modification. All covalent conjugation chemistry is done by standard carbodiimide chemistry, which links all carboxylic acid groups to primary amine groups on the enzymes to BSA. By creating such a highly crosslinked network, the conformational entropy of the interlocked enzymes is decreased. Thus, this one-pot two-layer method provides enzymes with enhanced stability, increased recyclability, and high retention in activity. When interlocked with BSA on BSA-Paper, laccase was 240 times more stable (half life = 180 days) at room temperature than unmodified laccase.

Lipase had a 26-fold increase in recyclability half-life (half-life 130 cycles). Glucose oxidase had a 6-fold increase in recyclability half-life (half life 11 cycles). In the next step, the chemistry will be carried out on cellulose nanoparticles as colloidal systems for a variety of applications. This approach is also applicable to other enzymes regardless of their molecular weight, isoelectric point, enzymatic activity, or other enzymatic properties, thus making it a powerful tool for creating novel enzyme-based paper devices that require enhanced stability at room temperature.

COLL 221

Fabrication of 1D photoreflective multilayered films by layer-by-layer assembly and transfer method

Arum Jung¹, *heroarm91@hanyang.ac.kr*, **Nari Ha**², **Myonghoo Hwang**³, **Bomin Kim**⁴, **Bongjun Yeom**¹. (1) *Hanyang University, Seoul, Korea (the Republic of)* (2) *Myongji University, Yongin, Korea (the Republic of)* (3) *Hanyang university, Seoul, Korea (the Republic of)* (4) *Chemical engineering, Hanyang university, Seoul, Korea (the Republic of)*

1D Photonic crystals with periodic multilayered nanostructures hold the limelight for the next generation optical devices. However, previous approaches have limitations such as selection of substrates due to relatively high processing temperature in the preparations of photonic crystal films. In this study we present fabrication method of 1D photoreflective films via layer-by-layer assembly and transfer method applicable to flexible substrates and for large-scale production. Two types of thin films with different refractive indices were prepared using layer-by-layer assembly onto soft substrates and those thin films were alternately transferred onto target substrates. We investigated the effect of adhesion between films and substrates are critical for successful transfer, and verified wavelength range of reflectivity can be largely tuned from visible to near IR. This fabrication method is expected to be applied in various applications such as optical sensors, displays, solar devices and so on.

COLL 222

Fabrication of drug-eluting coatings by harnessing electrostatic interactions with native protein films

Sanjana Gopalakrishnan¹, *sgopalakrish@chem.umass.edu*, **Li-Sheng Wang**², **Yi-Wei Lee**³, **Vincent M. Rotello**⁴. (1) *Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States* (2) *Chemistry, University of Massachusetts Amhers, Amherst, Massachusetts, United States* (3) *Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States* (4) *Univ of Massachusetts, Amherst, Massachusetts, United States*

Antimicrobial coatings have emerged as a solution to prevent bacterial contamination, particularly in the case food packaging materials, water treatment membranes and

medical devices and implants. Infections caused by bacterial contamination of medical devices such as stainless-steel IV poles and implants, is a serious healthcare problem. Designing a biocompatible coating with antibacterial activity is crucial for limiting contamination, especially on medical devices and implants to prevent the spread of infections in patients. Protein-based materials have come forth as potential candidates for designing biocompatible and sustainable biomaterials. Translating protein precursor properties into protein films is essential for various biological applications such as tissue engineering and controlled drug release. Herein, we demonstrate the use of charged protein films that can be used to load and control release antibiotics via electrostatic interactions. These drug-loadable protein films are prepared by an additive-free strategy, utilizing a fluorinated media to thermally treat and stabilize the coating. They can be used to design conformal coatings on complex three-dimensional substrates. Moreover, they are stable in physiological conditions, sustainable and biodegradable thus making them well suited for medical implants.

COLL 223

Facile synthesis of iron oxide nanoparticles using atmospheric-pressure microplasmas

Lee Ching Yu, georgelee81@gmail.com. Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

Iron oxide nanoparticles (NPs) have been reported a new class of novel nanomaterials with exceptional properties including superior magnetic properties, biocompatibility and high surface area, and could be potentially used for emerging applications including biosensing, drug delivery, pollutant treatment, energy storage and catalysts. While co-precipitation method is the most common technology to produce Iron oxide nanoparticles, it is still difficult to control the particle size and size distribution in a simple manner. Moreover, toxic chemicals and strong reducing agents such as NaOH and NaBH₄ are usually needed. Consequently, it is required to develop a simple, green and scalable method to produce iron oxide NPs to realize their commercialization. Here we present a facile synthesis iron oxide NPs using a novel atmospheric-pressure microplasma-assisted electrochemistry. Microplasmas are defined as gaseous discharges formed in electrode geometries where at least one dimension is less than 1mm. Additionally, microplasmas can be operated with an aqueous solution as an electrode. Plasma beam were ignite on the interface of the solution and cathode. Energetic species formed in the microplasma are capable of initiating electrochemical reactions and nucleating particles in solution without the need for a chemical reducing agent. In our experiments result, we found nanoscale iron oxide NPs can be synthesis using atmospheric-pressure-microplasma-assisted electrochemistry. Furthermore, we synthesis Fe₃O₄/Carbon materials composite under the microplasma system as multifunctional nanostructures. As-produced samples were characterized by XRD, Raman UV-Vis spectroscopy, and use TGA and SQUID to measure the component and magnetic property. We found that process parameters including plasma current, time

and precursor concentrations are key factors to control the production yield and particle morphologies.

COLL 224

Fast dopant migration in Mn:CdS/CdZnS/ZnS core/shell/shell quantum dots

*Elan Hofman*¹, ejhofman@syr.edu, *Zhijun Li*², *Andrew H. Davis*¹, *Weiwei Zheng*¹. (1) *Chemistry, Syracuse University, Syracuse, New York, United States* (2) *Chemistry, Syracuse University, Syracuse, New York, United States*

Doping by introducing transition metal ions into host lattice is an efficient strategy to modify and/or introduce new properties of nanocrystals. The final properties of doped quantum dots (QDs) highly depend on the dopant sites because of the distance-dependent host-dopant coupling. Recent discovery of dopant migration inside core/shell QDs provide a new way to fine tune the properties of doped QDs. Although the dopant ion migration was found to be thermodynamically driven in CdS/ZnS core/shell QDs, whether the dopant migration can be further controlled by intentionally inserted shell(s) with less size mismatch with dopant is still unknown. In this work, we aim to control the Mn dopant migration rate and distance through the introduction of different thicknesses of CdZnS alloyed shell in CdS/CdZnS/ZnS core/shell/shell QDs. The radial position of the Mn inside the CdS/CdZnS/ZnS QDs was monitored by the Mn photoluminescence (PL) peak because Mn PL is very sensitive to the shell applied pressure (proportional to shell thickness) based on the spherically symmetric elastic continuum model. It was found that upon growth of thicker CdZnS alloyed interface, the dopants were able to migrate further away from the CdS core resulting in a smaller redshift in Mn PL. Furthermore, the delocalization of core excitons into the CdZnS shell provides further opportunity to finely control the CdS PL position and the CdS to Mn PL ratio.

COLL 225

Functionalized nanodiamonds in the investigation of aggregation phenomena

Lewis Lott, lq10@students.desu.edu, *Cherese Winstead Casson*. *Chemistry, Delaware State University, Dover, Delaware, United States*

Nanodiamonds (NDs) have gained increasing interest in the field of biomedical applications due to their low cytotoxicity, versatile surface chemistry, and intrinsic biomarker capabilities. Unfortunately, NDs suffer from severe aggregation phenomenon due to the myriad functionalities existing on the ND surface. This work is centered on a method to disaggregate NDs and increase the surface area. Impurities on the surface of NDs were removed using HNO₃ and H₂SO₄ to eliminate weak van der Waals interactions. Subsequent surface modification of the ND was then accomplished via covalent bonding between the biopolymer, chitosan (CS), and the carboxylated ND (ND-COOH) surface. The surface coverage of the ND surface by CS was studied by modifying the ratios between the ND-COOH and CS (w/w%). Fourier Transform infrared

spectroscopy (FTIR) showed characteristic bands of CS (3429 cm⁻¹ due to -OH and -NH groups in chitosan, 2902 cm⁻¹ attributed to C-H bands, 1656 cm⁻¹ due to amide band C-O stretching, along with N-H deformation, and 1592 cm⁻¹ due to the characteristic peak of the NH₂ groups). Modified nano-diamond chitosan composites (ND-COOH-CS) were also studied using zeta potential analysis (ZPA), particle size analysis (PSA), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). Stability of the nanodiamond dispersions were shown to be achieved as evidenced by the increase in zeta potential.

COLL 226

Generation of anisotropic gold and Au-Pd bimetallic nanoparticles on functionalized surfaces

Veronica Gerios, vgerios@umich.edu, Aileen Peer, Krisanu Bandyopadhyay. Department of Natural Sciences, University of Michigan - Dearborn, Dearborn, Michigan, United States

Variations in ratio of gold and palladium salt solutions (HAuCl₄ and K₂PdCl₄, respectively) when adsorbed and reduced on functionalized silicon and indium tin oxide (ITO)-coated surfaces have led to differences in catalytic ability of the resulting *in situ* generated bimetallic gold-palladium nanoparticles. Atomic force microscopy (AFM) has revealed an apparent change in the morphology of the nanoparticles in addition to an increase in size and number when the solution ratio of K₂PdCl₄ increases relative to HAuCl₄. The catalytic properties of these nanoparticle arrays were assessed electrochemically through the oxidation of multiple alcohols such as ethanol and ethylene glycol. Cyclic voltammetry studies revealed an enhanced catalytic conversion of ethylene glycol when the ratio of palladium increased relative to gold. Other techniques were also utilized in order to further understand the properties of these bimetallic nanoparticles. Zeta potential measurements traced the change in surface charge throughout the synthesis process. Additionally, UV-Visible (UV-Vis) spectroscopy was used to observe the change in optical properties before and after the reduction of the surface-bound Au and Pd ions. Lastly, X-ray photoelectron spectroscopy (XPS) was used to measure the elemental composition of the mixed nanoparticles. Further, preliminary results involving the anisotropic growth of gold nanoparticles showed possible increased catalytic ability.

COLL 227

Highly anisotropic PtCu alloy nanoframes used as efficient electrocatalysts for oxygen reduction and methanol oxidation

Xiaoya Cui, xcui004@e.ntu.edu.sg, Zhicheng Zhang, Hua Zhang. School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

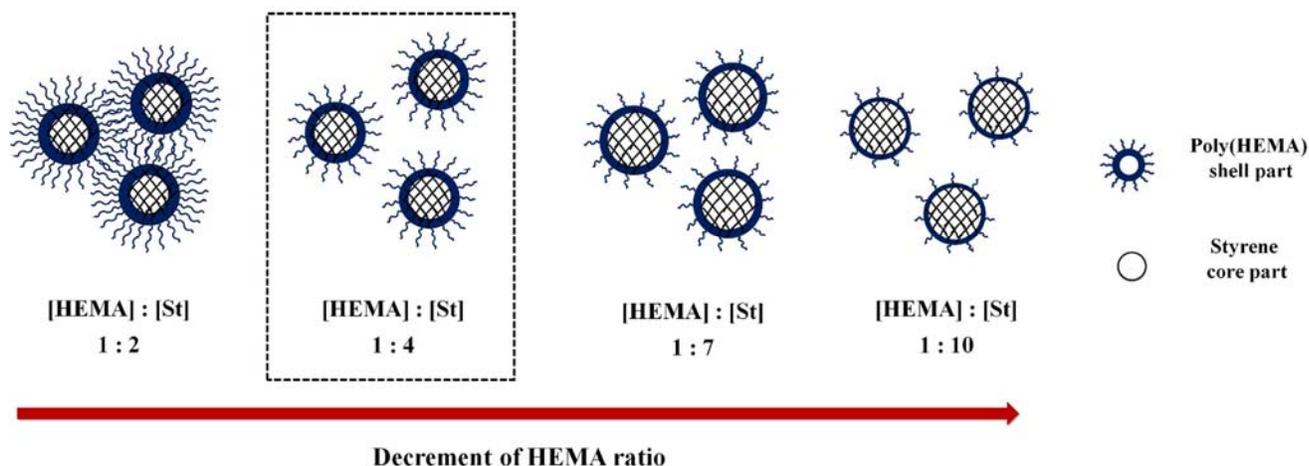
Noble metal nanoframes with highly open architectures have attracted increasing research interest recently owing to their inherent physical and chemical properties originating from their large surface area-to-volume ratio, three-dimensional accessible surface and reduced consumption of noble metals. Here, we report a simple one-pot hydrothermal method to synthesize highly anisotropic PtCu nanoframes (NFs) with nanothorns selectively protruding from the edge or vertex. The time-dependent experiment showed that the pure Cu nanodecahedra were first formed. Then the galvanic replacement reaction between Cu nanodecahedra and Pt precursors in the solution, and the subsequent site-specific co-deposition of Pt and Cu atoms are responsible for the formation of highly anisotropic PtCu NFs. Because of their highly anisotropic nature, structural defects, and the synergistic effect between different components, the PtCu NFs exhibit excellent electrocatalytic activity toward the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) under alkaline conditions, as compared to the commercial Pt/C catalyst and previously reported PtCu nanostructures. We believe our synthetic strategy will open up exciting opportunities for the rational design and synthesis of highly anisotropic noble metal alloy nanoframes, which could have various promising applications.

COLL 228

High-performance shear thickening behavior of a colloidal suspension of core-shell structure particles originated by inter-particle hydrogen bonding

Hoon Soo Son¹, *shshs0909@gmail.com*, **Kyoungho Kim**¹, **Jun Hyeong Kim**², **Kwan Han Yoon**², **Young Sil Lee**³, **Hyun-Jong Paik**¹. (1) *Polymer Science and Engineering, Pusan National University, Busan, Korea (the Republic of)* (2) *Department of Chemical Engineering, Kumoh National Institute of Technology, Gumi, Korea (the Republic of)* (3) *Industry-Academic Cooperation, Kumoh National Institute of Technology, Gumi, Korea (the Republic of)*

Shear thickening (ST) behavior is a non-Newtonian flow behavior which can reversibly exhibit a viscosity increase under strong impact. Shear thickening fluid (STF) is a well-dispersed colloidal fluid that shows the ST behavior. The spherical polystyrene nanoparticles with poly(hydroxyethyl methacrylate) shells (PS-PHEMA NPs) were prepared as the STF component and the influence of the structural characteristics of PS-PHEMA NPs -on the rheological properties of STFs was investigated. PS-PHEMA NPs, which indicate the narrow size distribution, were synthesized using surfactant-free emulsion polymerization and were dispersed into ethylene glycol, forming STFs. We searched for the optimum St/HEMA ratio on PS-PHEMA nanoparticles that can exhibit the highest ST effect. For this, various PS-PHEMA NPs were synthesized according to the ratio of St and HEMA ($[St]/[HEMA] = 2/1, 4/1, 7/1, 10/1$). We found that when St/HEMA was 4/1, the PS-PHEMA NPs exhibited a strong ST effect with the maximum viscosity up to 2800 Pa s. In this study, we could control structure properties of particles that could affect rheological property. The results imply that the hydroxyl groups and the charged groups on the particle surface have a critical influence on the rheological behavior of STFs.



Scheme1. PHEMA - PS particles according to monomer ratio

COLL 229

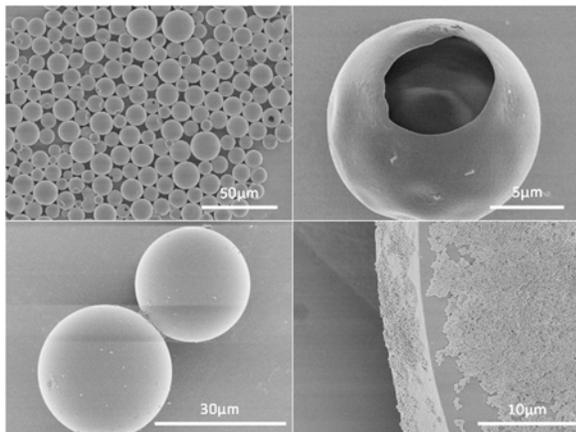
Hollow particles templated from Pickering emulsion and its application in coating shrinkage reduction

Xue Wang, 1572759395@qq.com, Guanqing Sun, Ren Liu. School of Chemical and Material Engineering, Jiangnan University, Wuxi, China

Shrinkage in UV-curable coatings due to replacement of Van der Waals intermolecular distance by covalent bonds is inevitable. Volume shrinkage occurring in the molding process is a major drawback for various applications, which leads to products warpage, shorten service life and spawn usage limitations as well as economic loss. Recently, expansion monomer and inert component have been widely used to reduce shrinkage in UV-curable coatings. However, these methods are either too complicated in practical uses or can only partly solve the problem and a general and easy method to reduce shrinkage is still lacking until now. Herein we introduce hollow particles with controlled elastic properties prepared by Pickering templates as a general route to solve this problem. The hollow particles not only can be used as reactable filler, but also can reduce the coating shrinkage due to their elasticity and expansionable structures.

In this work, reactable elastic hollow particles with adjustable and controllable wall thickness were fabricated by one-step Pickering emulsion with UV photopolymerization(OPEUP). The oil phase was composed of butyrolactone as solvent, glycidyl methacrylate(GMA) and 1,6-hexanediol diacrylate(HDDA) as reactants, and photoinitiator. After forming the Pickering emulsion stabilized by silica nanoparticles, UV light was applied to initiate the interfacial polymerization within a few seconds. As a result, OPEUP hollow particles with shell thickness from 200 nm to 5 μm can be successfully obtained by controlling the reactant and solvent ratios. The elasticity of the hollow particles can be controlled by adjusting reactant composition.

The morphology and structure of the hollow particles can be characterized from SEM images. The nanoindentation measurements indicate that hollow particles obtained show controllable mechanical strength with higher shell thickness. This unique property of the as-prepared hollow particle enables its potential uses in reducing volume shrinkage in UV-curable coatings.



COLL 230

Impact of interfacial and bulk interactions between novel amphiphilic hydroxypropyl cellulose derivatives and bile salts on lipid digestion

*Jennifer Zornjak^{1,2}, Diana Novo⁴, Kevin J. Edgar^{3,2}, **Cristina Fernandez Fraguas^{1,2}**, cfraguas@vt.edu. (1) Food Science and Technology, Virginia Tech, Blacksburg, Virginia, United States (2) Macromolecules Innovation Institute, Virginia Tech, Blacksburg, Virginia, United States (3) Sustainable Biomaterials, Virginia Tech, Blacksburg, Virginia, United States (4) Chemistry, Virginia Tech, Blacksburg, Virginia, United States*

Lipid digestion is a multistage process that relies up several interfacial and colloidal mechanisms to optimize lipid enzymatic hydrolysis (lipolysis) and transport processes. The adsorption of bile salts (BS) onto the oil-water interface of emulsions is a critical step for the progression of duodenal lipolysis. Hence, lipid digestion could be controlled ultimately by limiting the access of BS to the lipid surface, either by designing interfaces that resist displacement by BS, or by sequestering BS in the duodenum. The non-ionic and surface-active nature of cellulose derivatives make them promising candidates to modulate lipid digestion. In order to investigate the potential of novel cellulosic nanoparticles (CN) to modulate lipid digestion at BS concentrations relevant to physiological conditions within the duodenum, the aim of this work is to study the interactions between novel CN and BS in two different scenarios that emulsions find on their passage through the duodenum, namely the interface and the bulk.

Novel amphiphilic nanoparticles of hydroxypropyl-cellulose (HPC) were prepared through mild, versatile olefin cross-metathesis chemistry. We used surface-analysis techniques to explore the formation of HPC-BS layers onto hydrophobic surfaces by means of sequential adsorption, as representative of interfacial interactions, and

simultaneous adsorption, to study the ability of HPC to bind BS in solution. Sodium taurocholate (NaTC) and glycodeoxycholate (NaGDC) were chosen as representative BS with different hydrophobicity degree. Results showed that novel HPC derivatives are more resistant to BS (NaTC and NaTDC) displacement than commercial HPC at high BS concentrations. The more hydrophobic NaTDC showed a greater displacement of HPC from the surface than NaTC. HPC-BS bulk interactions seemed to impact the ability of HPC-BS complexes to disrupt BS adsorption at the hydrophobic surface. These findings provide valuable information on how commercial cellulose derivatives can be tailored and exploited into both novel food and pharmaceutical matrices to modulate lipid digestion.

COLL 231

***In vivo* antitumor effect of anti-Mammaglobin-A antibody conjugated to (-)-epicatechin loaded chitosan nanoparticles in a murine model of breast cancer**

Adriana Guadalupe Perez Ruiz¹, ydraperu@gmail.com, Ivonne María Olivares Corichi¹, Flora Adriana Ganem Rondero², José Rubén García Sánchez¹. (1) Escuela Superior de Medicina, Sección de Estudios de Posgrado e Investigación, Instituto Politécnico Nacional, Mexico, Mexico (2) División de Estudios de Posgrado (Tecnología Farmacéutica), Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, Cuatitlán Izcalli, Estado de México, Mexico

Breast cancer is the most frequently occurring cancer in women from Mexico and the world. The search of new therapeutic strategies against this cancer has focused on natural products, such as polyphenols, specifically flavonoids. In this context, our group has shown that (-)-epicatechin (a flavonoid) has an antiproliferative effect on cell lines of breast cancer. However, flavonoids are molecules typically prone to degrade when exposed to physical, chemical and biological factors, which limits its activity *in vivo*. Therefore, in this study we focus on developing and characterization (-)-epicatechin loaded chitosan nanoparticles (EC-Nps) and (-)-epicatechin loaded chitosan nanoparticles conjugated with antibody Mammaglobin-A (EC-MamA-Nps) for to evaluate their anticancer activity *in vivo*. The effects of these nanoparticles on ROS production and apoptosis induction in the tumour were investigated too. Methods: Nanoparticles were prepared by the supramolecular self-assemble process followed by anti-Mammaglobin A antibody conjugation was do using carbodiimide chemistry. The nanoparticles obtained were characterized by size, polydispersity index, Z potential, Fourier transform infrared spectroscopy and the morphology was established by confocal microscopy. The conjugation of antibody to nanoparticles was determindes by SDS-PAGE. Antitumoral effect was evaluate in a syngeneic transplant model on BALB/c mice. ROS production in tumours was determined by the values of biomarkers of oxidative damage such as carbonyl groups, quantification of formazan by nitroblue tetrazolium reduction (NBT), malondialdehyde (MDA), thiobarbituric acid reactive substances (TBARS), also the activity of glutathione peroxidase (GSH-Px) was analyzed. Finally, DNA fragmentation assay and caspase activation was performed to determine the induction of apoptosis

Results: We obtained nanoparticles with size of 200 nm, zeta potential negative, IP smaller than 0.2 and morphology was spherical shape. And eventually, the differences in biomarkers of oxidative damage (MDA, TBARS and NBT) and decreasing of GSH-Px activity were observed in tumours of mice treated with EC-MamA-Nps.

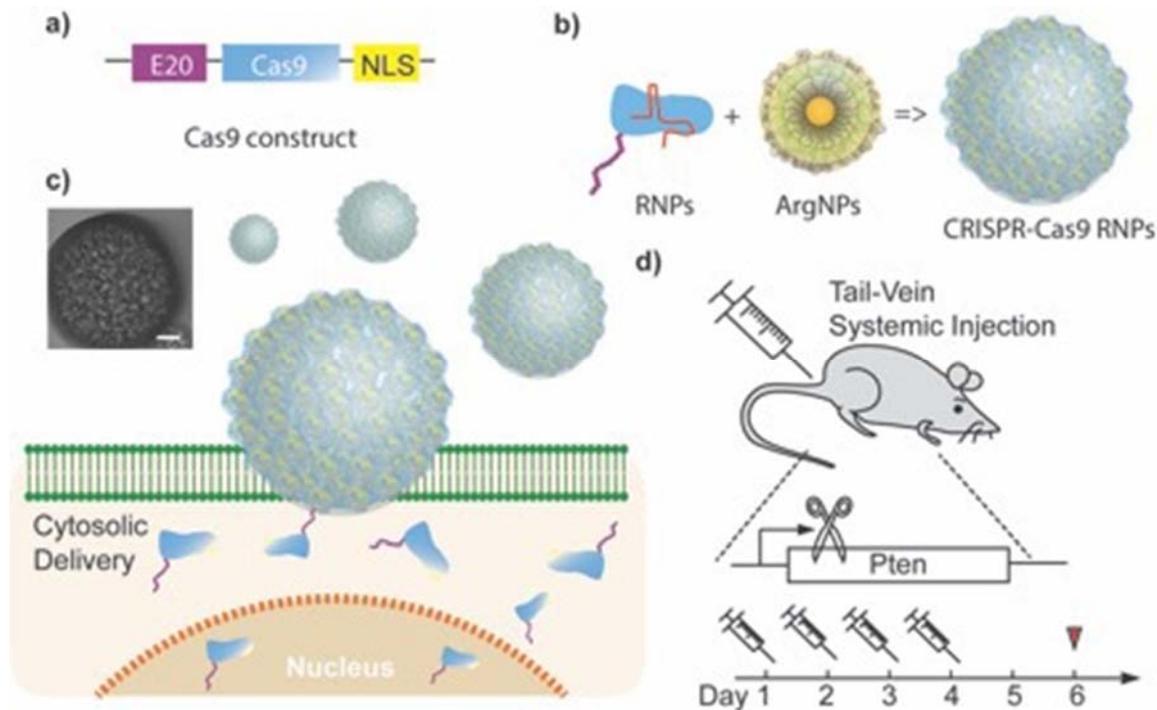
Conclusion: The data obtained in this study, suggest that the antitumor activity of nanoparticles EC-MamA-Nps is mediated by an induction of apoptosis and increase in the production of ROS.

COLL 232

***In vivo* gene editing in mice through systemic delivery of CRISPR/Cas9-ribonucleoprotein**

Yi-Wei Lee¹, yiweilee@umass.edu, David Luther², Yuanchang Liu⁴, Laura Castellanos⁵, Joseph Hardie⁶, Richard W. Vachet³, Vincent M. Rotello¹. (1) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (3) Univ of Massachusetts, Amherst, Massachusetts, United States (5) Chemistry, UMass Amherst, Amherst, Massachusetts, United States (6) University of Massachusetts Amherst, Amherst, Massachusetts, United States

Therapeutic gene editing through delivery of CRISPR-Cas9-ribonucleoprotein (RNP) provides vast opportunities in treating genetic diseases. Several systemic administrations have been attempted through viral vector delivery in the past, but all have suffered from induced immunogenicity. CRISPR-Cas9 protein delivery has been recognized as an effectively permanent genomic DNA editing strategy due to its nonreplicable process offering improved specificity. However, one hurdle in the application of the CRISPR system for human medicine is *in vivo* delivery: there has been no systemic CRISPR-Cas-RNP delivery reported thus far. Herein we report the delivery of Cas9-RNP into mice through systemic tail-vein injection, achieving up to >8% gene editing in liver and spleen.



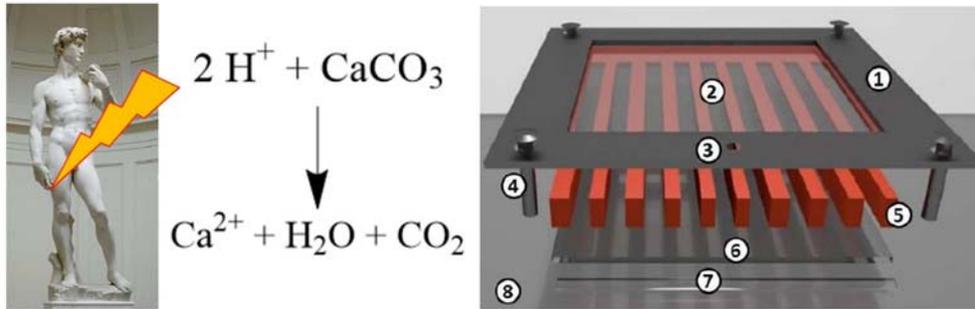
COLL 233

Infiltration and crystallization behavior of calcium carbonate precursor formulations in porous materials

Andra-Lisa M. Hoyt^{1,2}, andra-lisa.hoyt@uni-konstanz.de, Helmut Cölfen¹. (1) Chemistry, University of Konstanz, Konstanz, Germany (2) Doctoral Fellow, German Federal Environmental Foundation (DBU), Osnabrück, Germany

Cultural heritage that consists of porous calcium carbonate minerals suffers many detrimental influences leading to material loss and structural decohesion. Nanolimes have emerged as a new source of tools for its preservation as an improvement upon traditional techniques. While their modes of action have been investigated on surfaces and consolidation depth via time-delayed destructive methods like microdrilling, immediate real time observation and investigation of these processes inside confined pore spaces haven't been reported.

We have developed a first prototype of a pore-imitating micro-comb test system (MCTS) for real time *in situ* observation of infiltration and crystallization processes in confined spaces via light microscopy (LM). This enables the investigation of new infiltration candidates under more realistic conditions without destroying original substrates. The MCTS was used to observe these processes for a commercially available nanolime and a newly prepared liquid calcium mineral precursor formulation based on complex coacervation.



Left - Michelangelo's David as example of carbonatic art suffering from detrimental influences (symbolized by lightning bolt). Center - Chemical dissolution of calcium carbonate in aqueous acidic conditions. Right – Pore-imitating micro-comb-testing system consisting of metal frame (1), glass platelets (2+6), an inlet for injection (3), screws for fixation (4), the micro-comb center piece (5), a reservoir for the infiltration liquid (7) and transparent base plate of the apparatus (8).

COLL 234

***In-situ* electron diffraction tracking fast oxidation of nickel nanoparticles at ambient pressure**

Jian Yu¹, 11426060@zju.edu.cn, Xun Zhang¹, Ya Wang¹, Yong Wang². (1) Zhejiang University, Hangzhou, China (2) Materials Science and Engineering, Zhejiang University, Hangzhou, China

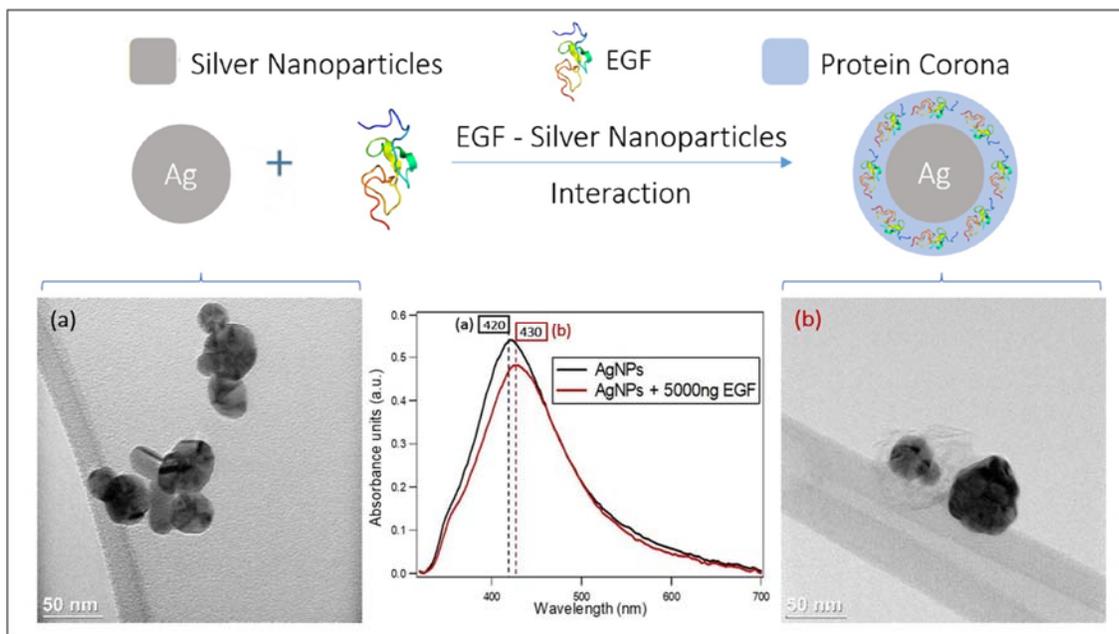
Real-time tracking the state of catalyst is essential for understanding catalytic mechanism, which usually involves complex structure and phase evolution. However, due to the lack of in-situ techniques with high time resolution, it is still a big challenge to follow the fast change of catalyst in a strong chemical reaction. Herein through transmission electron microscopy (TEM) equipped with high-speed camera and gas cell system, we developed an in-situ electron diffraction method, which could effectively obtain the structural information at ambient pressure with millisecond time resolution. As an example, the millisecond oxidation kinetics of nickel nanoparticles in oxygen was obtained by this method. The developed approach in this study can be readily applied to monitor the catalyst in other severe reactions.

COLL 235

Interaction of silver nanoparticles with epidermal growth factor (EGF) in physiological media: Evaluation for their potential use in systems that improve the regeneration of epithelial tissues

Luis Palomino¹, luispalomino026@gmail.com, Sarah Carney², Miguel R. Gakiya¹, Andrew Camardo², Anand Ramamurthi², Juan C. Rodriguez-Reyes¹. (1) Department of Bioengineering and Chemical Engineering, Universidad de Ingeniería y Tecnología - UTEC, Lima, Lima, Peru (2) Department of Biomedical Engineering, Cleveland Clinic, Cleveland, Ohio, United States

The special properties of silver nanoparticles (AgNPs), such as their ease of synthesis, biocompatibility and antibacterial activity, have attracted attention for their use as carriers of therapeutic agents in the field of tissue engineering and regenerative medicine. The implementation of these technologies requires the understanding of the interaction nanoparticle-biomolecule, especially to determine the biological (for example, therapeutic) activity of said biomolecules and evaluate their safe use. Here, we present a methodology to test the interaction of AgNPs with epidermal growth factor (EGF), which is of interest for the regeneration of epithelial tissue. The stability of AgNPs-EGF structures in physiological conditions (using PBS medium at pH 7.4 and 37 Celsius degrees) and using different molar ratios is evaluated using FTIR and UV-Vis spectroscopy, as well as DLS and zeta potential measurements. Since for tissue regeneration it would be ideal to take advantage of the antibacterial properties of AgNPs, we compare the activity of nanostructures in culture of *Escherichia coli*. It is expected that this work will contribute to the development of new materials for the regeneration of epithelial tissues.



COLL 236

Investigating the impact of nanoparticle shape on single nanocrystal photophysics

Jeffrey J. Peterson, peterstonj@geneseo.edu, **Brandon Mehlenbacher**. *Chemistry, SUNY Geneseo, Geneseo, New York, United States*

The blinking kinetics of differently shaped CdSe nanoparticles (NPs), zero-dimensional quantum dots, one-dimensional quantum rods, and two-dimensional quantum platelettes, have been characterized by single molecule (SM) fluorescence spectroscopy. The study uses a novel approach in which NPs are synthesized and SM

measurements performed without ever exposing them to ambient oxygen, thereby preserving the NP surface and enabling SM characterization without extensive surface modifications. The impacts of NP surface area and confining dimension on various photophysical parameters associated with blinking processes, including power law exponents, fall-off times, and grey-state sampling, will be presented. The work provides a unified investigation of the role of NP shape (spherical vs. cylindrical vs. elliptical) and helps provide a clearer picture the fundamental factors that define NPs' optical properties.

COLL 237

Investigation of selective growth of ALD alumina on functionalized HOPG surfaces

Mikhail Trough¹, matrough@mtu.edu, **Isobel Wentworth³**, **Timothy R. Leftwich²**, **Kathryn A. Perrine¹**. (1) Department of Chemistry, Michigan Technological University, Houghton, Michigan, United States (2) Department of Materials Science and Engineering, Michigan Technological University, Houghton, Michigan, United States (3) Department of Chemical Engineering, Michigan Technological University, Houghton, Michigan, United States

Nanostructured heterogeneous catalysts are designed to increase activity and selectivity of reactions. Currently catalysts are designed using calcination and impregnation methods, which result in poor uniformity due to a lack of control of the size, structure and composition and lead to unwanted by-products in a catalytic reaction. In order to improve on catalyst design and control of the growth at the nano- and meso-scale, it is vital that surface chemical approaches are understood, where tailored functionality is incorporated on the atomic scale. Atomic layer deposition (ALD) is a vapor deposition technique that utilizes *surface chemical reactions* to grow metal oxides from inorganic precursors one atomic layer at a time. Atomic control is achieved through self-limiting surface reactions, where the surface functional groups initiate the first step in the deposition process.

We investigate how surface chemical reaction sites result in selective deposition of aluminum oxide (Al_2O_3) using ALD. The highly ordered pyrolytic graphite (HOPG) surface is used as a model support for Al_2O_3 growth. The HOPG surface is a multilayered graphene surface that possesses interfacial ordering of sp^2 carbon atoms making their terraces relatively inert towards adsorption of weakly binding molecules, albeit their defects remain highly reactive. We show how different treatments of the HOPG surface result in different growth of surface morphologies of Al_2O_3 . The surfaces are analyzed using X-ray photoelectron spectroscopy, Fourier transform-infrared spectroscopy, Raman spectroscopy and mapping, scanning electron microscopy and atomic force microscopy. Our studies suggest that the growth of Al_2O_3 on functionalized HOPG using ALD is achieved by controlling the morphology of functional sites. The knowledge learned using this proof-of-concept method provides a fundamental

understanding of surface functionalization leading to metal oxide growth using bottom-up approaches.

COLL 238

Kinetic study of the adsorption of methylene blue onto chitosan: Evidence for non-Arrhenius behavior

Alexandre H. Pinto, apinto2@ithaca.edu, Julian Kellner-Rogers. Department of Chemistry, Ithaca College, Ithaca, New York, United States

The water contamination is a serious environmental issue, among the main contaminants found in the aquatic environment are synthetic dyes. Adsorption of the dyes onto safe and unharmed adsorbents has proven to be a clean and effective method to remove the dyes from wastewater. A promising adsorbent is chitosan, which is a natural polymer containing amino (NH_2) groups in the polymeric chain. Chitosan is derived from chitin, which is the second most abundant natural polymer after cellulose, it is found in crustacean shells, such as crabs and prawns. The abundance of chitin and its straightforward deacetylation conversion process make chitosan a cost-effective material for several applications, such as drug delivery, cosmetic products, tissue engineering, and food processing. In the present research, chitosan is used as adsorbent for the removal of the textile dye methylene blue (MB) from simulated wastewater in order to verify how effective this removal process can be at different temperatures. The experiments revealed that the contact between MB and chitosan gives rise to an additional peak in the visible absorption spectrum. This phenomenon is called metachromasy and happens due formation of MB aggregates, in addition to MB single molecules. The adsorption process of MB molecules and aggregates could both be described by a second order kinetics model. The Arrhenius graph plotted from the rate constants obtained for each temperature indicated that both MB molecules and aggregates do not follow an Arrhenius behavior, instead, they present quadratic dependence on Arrhenius graph, where the activation energy of the adsorption process is temperature dependent. The coexistence of the MB molecules and aggregates decreases the efficiency of the dye removal process by chitosan, since the two MB species start to compete for the adsorption sites present in the chitosan surface, resulting in an incomplete dye removal.

COLL 239

Kinetics of amino acid induced aggregation of silver nanoparticles

Karen I. Peterson¹, kpeterson@mail.sdsu.edu, Josiah Smith², David P. Pullman². (1) San Diego State Univ, San Diego, California, United States (2) San Diego State University, San Diego, California, United States

In order to understand the nature of silver nanoparticles in biological systems, it is important to characterize their surface properties and the transformations that take

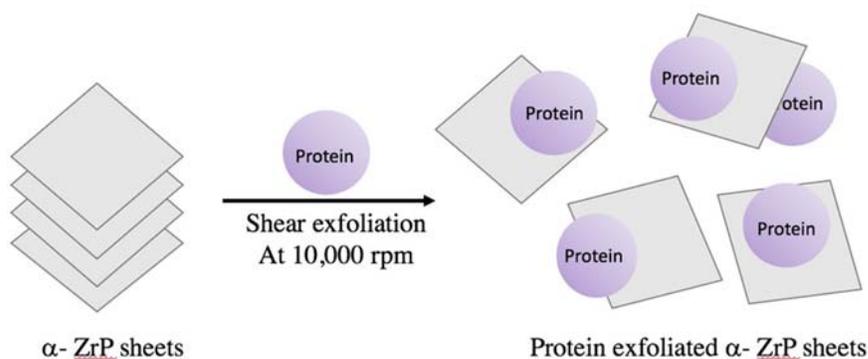
place in the presence of adsorbing solutes. Previously, we carried out a detailed kinetic study of the effects of sodium chloride, which not only increases the ionic strength of the solution, but also interacts chemically with the surface of the nanoparticles, lowering the surface charge. In this system, oxidative decomposition of the nanoparticles competes with the aggregation process. More recently, we have turned to amino acids, specifically histidine, lysine, and arginine, which neither affect the ionic strength substantially, nor chemically react with the AgNP surface. We have found that these amino acids physically adsorb to the surface and induce aggregation at rates which increase in the order listed, correlating with the basicity of the side chain. More interestingly, the aggregation mechanisms of these systems appear to differ from each other. Histidine-induced aggregation is second order with a relatively slow rate, but lysine- and arginine-induced aggregation, after an initially fast rate, levels off to a slower rate comparable to that of the histidine. We are working on a procedure to independently monitor the time evolution of the monomer, dimer, and higher aggregates. Our goal is to elucidate the mechanistic differences among these amino acids

COLL 240

Kitchen Chemistry 102: Exfoliation of alpha-zirconium phosphate with proteins in a blender as an alternative to exfoliation by tetrabutyl ammonium hydroxide

Mansi Malhotra¹, mansi.malhotra@uconn.edu, Clive L. Baveghems², Challa V. Kumar^{3,2}. (1) Chemistry, University of Connecticut, Willimantic, Connecticut, United States (2) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (3) Univ of Connecticut, Storrs Mansfield, Connecticut, United States

Exfoliation of alpha- zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α -ZrP) is previously attained by treatment with tetra-n-butylammonium (TBA) hydroxide. While this is excellent for most applications, biological end uses of this 2D material require biofriendly alternative. Toward this goal, we developed a novel method to exfoliate alpha-ZrP using Bovine Serum Albumin (BSA) and a simple shear reactor, such as a kitchen blender. The exfoliation was rapid and essentially complete in few hours when a commercial shear reactor was used. The quality of the exfoliated nanoplates was followed by powder X-ray diffraction which indicated a rapid loss of the peak corresponding to the 7.6 Å peak and confirmed by electron microscopy. In addition to BSA, other proteins such as b-lactoglobulin, ovalbumin, lysozyme, glucose oxidase, and haemoglobin also induced exfoliation and the highest exfoliation efficiency has been achieved with ovalbumin (» 90% exfoliation efficiency at room temperature). The exfoliated alpha-ZrP nanoplates have been used as a biological matrix for building artificial light harvesting complexes which were very stable to photodegradation than without alpha-ZrP. This biofriendly material is being tested for applications such as drug delivery as well.



Exfoliation of alpha-zirconium phosphate with protein by using shear force.

COLL 241

Laundering study of current and future FRACU (Flame-Resistant Army Combat Uniform) candidates

Pearl Yip, *pearl.w.yip.civ@mail.mil. Army, NSRDEC, Natick, Massachusetts, United States*

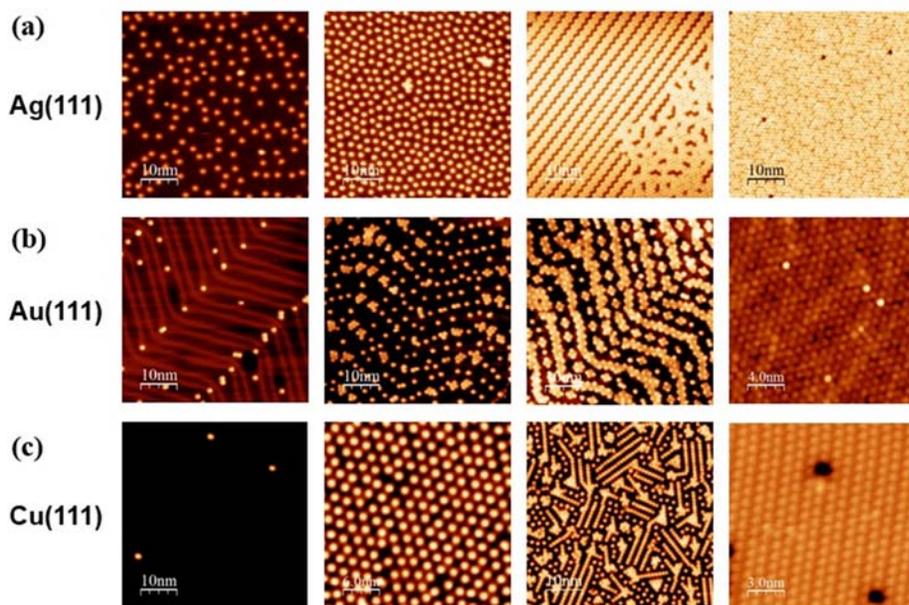
The ability to maintain flame retardancy after repeated laundering cycles is critical for flame resistant (FR) military fabrics and uniforms. The objective of this effort was to develop independent in-house testing methods to study the effect of laundering on the FR performance of these FR treated fabrics. The results from these methods could help evaluate and select future replacement candidates for the costly Defender M fabric, which is currently used to make the Flame Resistant Army Combat Uniforms (FRACUs) for the U.S. soldiers. The American Association of Textile Chemists and Colorists (AATCC) laundering test method AATCC 135 is the laundering method used to study these fabrics to evaluate the durability of their treatment against home laundering agitation for up to 50 cycles of washing and drying. Multiple characterization techniques including the Simultaneous TGA (thermal gravimetric analysis) -DSC (differential scanning calorimetry), SEM (scanning electron microscopy), PY (pyrolysis)-GC (gas chromatography) MS (mass spectroscopy), as well as the vertical flame test ASTM D6413 are used in this project to determine the consequences of laundering on the FR performance of these fabrics before and after launderings.

COLL 242

Long range interaction between corannulene molecules on (111) surface of noble metals

Xiaojie Wen, *xzwen@pku.edu.cn, Kai Wu. College of Chemistry Molecular Eng, Peking University, Beijing, China*

Corannulene ($C_{20}H_{10}$, COR), a fragment of C_{60} , has received a lot of academic interest due to its bowl-like stereo structure and its unique aromatic property. The assembly behaviors of COR on various metal surfaces with high coverage (monolayer) have been investigated, however, low coverage assembly are not explored. Using scanning tunneling microscopy (STM), here we report that highly dispersed superstructures of corannulene are found on Au(111)/ Ag(111)/ Cu(111) surface with low coverage which are mediated by substrate surface-state electrons. What's more, the separations of nearest neighbor molecules match distance of half-multiples of the Fermi wavelength of the metal. When dosing more COR on Au(111)/ Ag(111), a 2 nm wide stripe pattern which is stabilized by dipole-dipole interaction is formed with COR pointing up in the middle and COR pointing down on two sides which does not exist on Cu(111) due to its high activity. The distance between the stripe also favors half-multiples of the Fermi wavelength of the substrate which imply long-range electronic interactions.



STM images of COR on (a) Ag(111); (b) Au(111); (c) Cu(111) from low coverage to high coverage (from left to right).

COLL 243

Magneto/plasmonic nanoliposomes for drug delivery applications: Synthesis and characterization

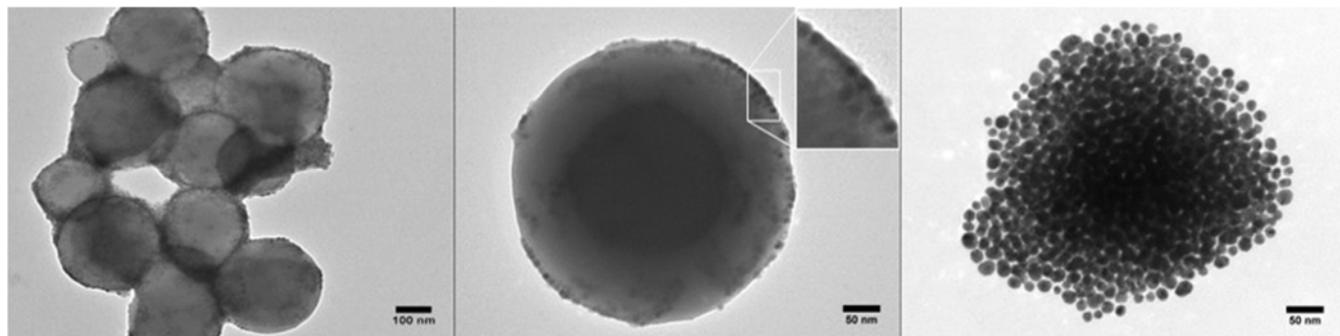
Gabriela Stiufiuc¹, gabi.stiufiuc@phys.ubbcluj.ro, **Stefan Nitica**³, **Valentin Toma**³, **Alin Moldovan**³, **Cristian Iacovita**², **Mihai Lucaciu**², **Rares Stiufiuc**^{2,3}. (1) Faculty of Physics, "Babes-Bolyai" University, Cluj-Napoca, Romania (2) Faculty of Pharmacy, University of Medicine and Pharmacy, Cluj-Napoca, Cluj-Napoca, Cluj, Romania (3) MedFuture

Research Center for Advanced Medicine, "Iuliu Hatieganu" University of Medicine and Pharmacy, Cluj-Napoca, Romania

Combining liposomes with different types of nanoparticles (magnetic, plasmonic) recently emerged as a very intriguing approach that holds the potential to generate biocompatible multifunctional nanovesicles for drug delivery applications. The importance of such nanohybrids resides in their ability to release the incorporated therapeutic agents in a very controllable and reproducible manner as a result of their interaction with several external stimuli (NIR lasers and/or magnetic fields). Owing to their amphiphilic character, the liposomes have the capacity to incorporate hydrophilic as well as hydrophobic molecules of interest.

In this letter we present an original new method developed in our laboratory for the synthesis of such hybrid nanoobjects: plasmonic liposomes, magnetoliposomes and plasmonic magnetoliposomes. Two strategies have been developed for the creation of the nanoobjects. Firstly, the plasmonic liposomal nanocarriers (PLiN) have been prepared by taking advantage of electrostatic interactions between small unilamellar cationic liposomes and negatively charged biocompatible gold nanoparticles. This allowed the synthesis of liposomes decorated on their outer surface with plasmonic nanoparticles. On the other hand, a completely different strategy has been developed for the synthesis of magnetoliposomes (MLip). In this case the hydrophobic/hydrophilic interactions between small SPIONs and neutral phospholipids have been used for MLips synthesis thus allowing the incorporation of hydrophobic SPIO nanoparticles into the liposomal lipid bilayer.

The as-synthesized liposomes have been analyzed by UV-Vis absorption spectroscopy, Photon Correlation Spectroscopy (PCS), Zeta Potential Measurements and Transmission Electron Microscopy (TEM), Hyperspectral Microscopy. Their plasmonic properties have been evaluated using SERS for excitation wavelengths ranging from UV to NIR (325-830 nm). The hyperthermic properties of the nanohybrids arising from their interaction with an external laser or a magnetic field have been assessed for NIR lasers (785 nm) and external magnetic fields with intensities ranging between 5 and 60 kA/m and frequencies between 100-400 kHz. The toxicity of the nanohybrids have been assessed in-vitro on different cell lines using the standard MTT assay.



COLL 244

Management of gold nanorod synthesis with poly(vinylpyrrolidone) of different molecular weights in minor concentration

Katherinne I. Requejo Roque, kirequejo@gmail.com, Anton Liopo, Eugene Zubarev. Chemistry, Rice University, Houston, Texas, United States

Gold nanorods (AuNRs) are anisotropic nanoparticles that have attracted great interest because of their unique optical properties and different dimensions that enable applications in sensing, imaging and therapy. Despite several investigations have reported the broad longitudinal surface plasmon resonance (LSPR) band tunability, few of them have focused on the synthesis of small nanorods in high yield. Here, we report a novel, reproducible and scalable protocol for the seedless synthesis of AuNRs with hydroquinone as weak reducing agent and poly(vinylpyrrolidone) (PVP) as additive. The polymer is introduced to growth solutions during synthesis for 100 mM of surfactant cetyltrimethylammonium bromide (CTAB). By using PVP of distinct molecular weights (5-360 kDa), the LSPR band is tuned from 850 to 1010 nm as a function of polymer addition time. Also, the original aspect ratio (length/width) for nanorods with size of 43 x 7 nm is reduced at different extents depending on the polymer molecular weight. It was found that PVP accelerates the growth rate of AuNRs by more than two times as the molecular weight increases. However, only the use of low molecular weight PVP such as 10 kDa produces AuNRs in high yield. The interaction of the polymer to the nanorod surface was determined by attenuated total reflectance (ATR) and X-ray photoelectron spectroscopy (XPS) analysis. It is suggested that PVP interacts with AuNRs through the oxygen atom of the carbonyl group. Moreover, the estimation of the average number of PVP chains per nanorod in solution indicates that around 30 molecules may interact with AuNRs and contribute to their stabilization. Because nanomolar concentration of PVP is utilized, it is expected that the polymer acts less like a reducing agent, as seen in traditional polyol synthesis, but as a templating group to stabilize the growing nanorods.

COLL 245

Manganese doped two-dimensional CdS/ZnS core/shell nanoplatelets

Andrew H. Davis, adavis11@syr.edu, Weiwei Zheng, Elan Hofman, Kevin Chen. Chemistry, Syracuse University, Syracuse, New York, United States

The ability to dope transition metal ions into non-magnetic semiconductors allows for the induction of new properties not pertaining to the original material. While the synthesis of doped 0-dimensional (0-D) quantum dots and 1-D nanorods and nanowires have been widely reported, transition metal ion doped 2-D nanocrystals have been less explored. In this study, we developed a one-pot synthesis of Mn²⁺ doped 2-D CdS nanoplatelets (NPLs). Furthermore, we synthesized ZnS shell passivated Mn:CdS/ZnS core/shell NPLs using a single-source shelling precursor (SSSP) method to improve

stability and optical properties including photoluminescent quantum yield (PL QY), tunable PL ratio between the host NPLs and Mn dopants. We found that lifetime, host-dopant energy transfer, and Mn-Mn interactions were dopant concentration-dependent. The SSSP method employs a single-source precursor, Zn(DDTC)_2 , that decomposes at relatively low temperatures, allowing for ZnS shell passivation with minimal NPL thermal degradation. Through dopant introduction and surface modification, we have synthesized not only the first doped 2-D Mn:CdS core NPLs, but also the first 2-D Mn:CdS-based core/shell NPLs with increased thermal, stability and enhanced optical properties.

COLL 246

Detection of the onset of aggregation as a function of pH of iron oxide nanopowder by dynamic light scattering

Lauren Szwast, lszwast@brookhaveninstruments.com. Brookhaven Instruments Inc., Holtsville, New York, United States

Automated measurement of effective diameter as a function of pH is fast and easy with the Brookhaven Instruments NanoBrook Omni and ZTU autotitrator. Given the great potential for applications using iron oxide, it is beneficial to understand the effect of chemical changes to the surface of the nanoparticle. The aim of this study was to determine if the onset of aggregation could be detected with a change in pH. Iron oxide nanopowder (Fe_3O_4) was used as received from SkySpring Nanomaterials, Inc. A solution was prepared by adding 5.8 mg of the commercially available iron oxide nanopowder to 20 mL of filtered MilliQ water. A 0.2 μm filter was used to filter the MilliQ water 3 times. The solution was then sonicated in a Branson 2800 low energy sonic bath for five minutes. The autotitrator was loaded with four reagents: 0.1 M nitric acid, 1 mM nitric acid, 0.1M potassium hydroxide, and 1 mM potassium hydroxide. All reagents were produced by Fluka Analytical. The suspension was tested from a pH of 2 to 12 in 2 pH unit steps. The solution was analyzed at each pH 5 times, each for 5 minutes per run using dynamic light scattering (DLS).

The onset of aggregation was detected between pH 4 and 6. The effective diameter of iron oxide nanoparticles was in the size range of 592 to 1430 nm by intensity in acidic solution pH. The effective diameter of iron oxide nanoparticles was in the size range of 1173 to 5009 nm by intensity in basic solution pH. With the use of Brookhaven Instrument's Particle Solutions software, it was clear that as the pH value increased, the effective diameter increased and the stability decreased.

The ability of the Brookhaven Instruments NanoBrook Omni Particle Size Analyzer and ZTU to detect the onset of aggregation in commercially available iron oxide nanoparticles and its ease of use with a quick sample preparation make it a useful tool in biomedical and bioengineering industries. This general method can be applied to many types of nanomaterials and can be customized to particular applications by incorporating different parameters such as time dependence or additive titrations like salts or dispersing agents. Many industries can be favorably supported by tools such as the NanoBrook Omni together with the ZTU.

COLL 247

Measurement of carbon black particle size using a disc centrifuge photosedimentometer

Lauren Szwast, lszwast@brookhaveninstruments.com. Brookhaven Instruments Inc., Holtsville, New York, United States

A Brookhaven Instruments disc centrifuge photosedimentometer (DCP) was used for the measurement of carbon black. Accurate results were obtainable for commercially available carbon black. Following a carbon black protocol provided by Brookhaven Instruments, the carbon sample was prepared. 10 mg of carbon black standard was weighed out into a vial and combined with EtOH. The suspension was sonicated in a low energy sonic bath to wet the sample. After the sample came to room temperature, Triton X-100 was added to the suspension. The suspension was then probe sonicated at 40% power and a 50% duty cycle for 10 minutes. The suspension was de-gassed in a sonic bath and then injected into the disc centrifuge photosedimentometer. The suspension was analyzed a minimum of 3 times a day for 3 days and was prepped once a day.

The results were very repeatable. The mean diameter was between 211-242 nanometers. The results were also consistent with the expected diameter for the standard. The standard was <500 nanometers. Carbon black is used in countless rubber materials including tires. It is used as a pigment in lacquers and inks. Disc centrifuge photosedimentometers have been used for more than a few decades by many industries and is the go-to technology for particle characterization for many of these industries.

COLL 248

Measurement of graphene particle size using laser obscuration time technique

Lauren Szwast, lszwast@brookhaveninstruments.com. Brookhaven Instruments Inc., Holtsville, New York, United States

Graphene is a carbon-based material that was discovered in 2003. Scientists hope to use this material to make touchscreens, water filtration systems, medicines, and batteries.

Laser diffraction was once considered the ideal method for characterizing particles in the micron size range. Laser diffraction requires the user to assume sphericity and to know their sample's refractive index. For accurate particle sizing, testing has shown that for particles which are not spherical, laser obscuration may be a more optimal choice. Laser obscuration is beneficial for samples that are transparent, semitransparent, agglomerates, or aggregates. Graphene nanoplatelets were evaluated to show the efficiency of the laser obscuration method using the Brookhaven Instruments MicroBrook EyeTech.

The graphene sample was prepared by combining 3.9 mg of sample with approximately

20 mL of filtered MilliQ water. The MilliQ water was filtered 3 times using a Pall 0.2 μ m sterile syringe polyethersulfone membrane filter. The suspension was sonicated in a Branson 2800 low energy sonic bath for ten minutes. Analysis was completed on the EyeTech instrument by performing a total of 3 measurements. Data was acquired over 9 minutes using 180 second cycles for both laser and image analysis. The data demonstrated the ability of the MircoBrook Eyetech to give repeatability in particle size for the graphene nanoplatelets.

COLL 249

Measurement of water partial molar volume in Aerosol-OT reverse micelles via microscopic imaging of the liquid surface

Corey Gallis¹, Zachary Rickard^{1,2}, John C. Deak¹, deakj2@scranton.edu. (1) Chemistry, University of Scranton, Scranton, Pennsylvania, United States (2) Sanofi, Swiftwater, Pennsylvania, United States

Partial molar volume measurements of water in AOT/isooctane reverse micelles were used to examine molecular interactions and structural aspects of the aggregate. Measurements were made using an inspection microscope to detect minute solution volume changes as a quantitative amount of water was added to the emulsion. This method is superior to traditional molar volume measurements that rely upon density measurements in that it is a direct measure of molar volume and makes no assumptions about the system. Experiments were performed over a range of reverse micelle size in order to assess how water interactions and surfactant packing are affected by the size of the reverse micelle. It was found that water in the reverse micelle is well described as two separate domains (bulk and interfacial waters) whose partial molar volumes are independent of reverse micelle size. Interfacial water has a lesser partial molar volume indicative of less hydrogen bonding interactions than the bulk water region. The thickness of the surfactant layer was also deduced from these measurements.

COLL 250

Mesoporous graphene oxide-zeolite composites for efficient dye removals

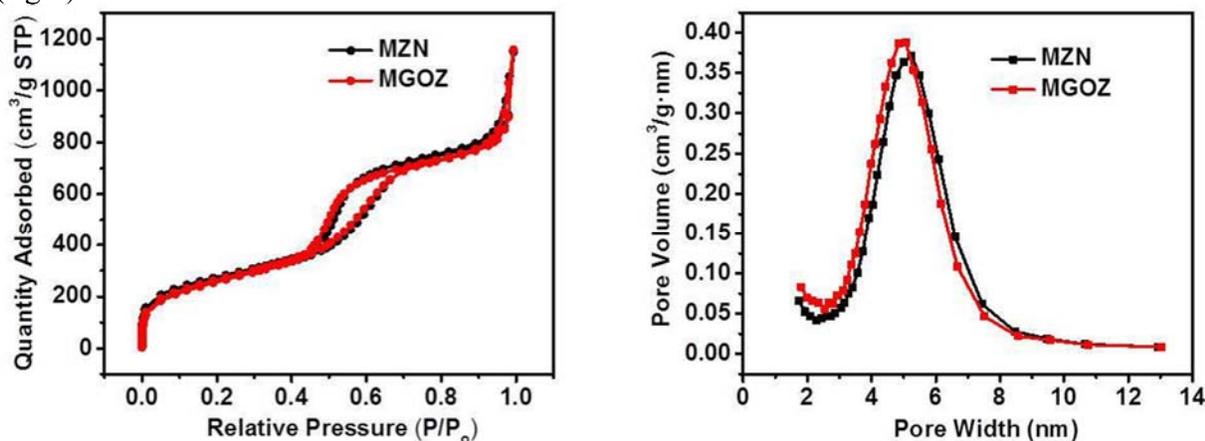
Yun-Jou Chang, clover5972@gmail.com, Yi-Chieh Chou, Zhi-Jyun Dai, Yi-Chun Yeh, Yi-Hsin Liu. Chemistry, National Taiwan Normal University, Taipei, TW, Taiwan

Mesoporous graphene oxide-zeolite (MGOZ) composites with high surface area (>900 m²/g) and large pore size (~5 nm) are employed to remove fluorescent dyes from aqueous solution. Environmental pollutants, including but not limited to non-biodegradable dyes, in wastewater cause sustainable threats to aquatic and marine life. During our recent advance in mesoporous zeolites, carbon-based nanocomposites demonstrate efficient separation (>95% within 10 min) of Rhodamine 6G (R6G) from diluted solution (0.01mM) via monitoring in absorption and emission spectroscopy. Kinetic and thermodynamic studies also suggest pseudo-second order model and very

large equilibrium constant upon monolayer adsorption in various pH ranges. The extended surface area and ordered mesoporosity can be also utilized to recycle noble metal ions (e.g. Ag^+ , Au^{3+} , Pt^{4+}) and reuse for economic purposes.



Comparison of 0.01mM R6G before (left) and after adsorption by MGOZ (middle) and MZN (right)



N_2 isotherms (left) and pore size distributions (right) of MGOZ and MZN at 77K

COLL 251

Micellar water characterization: A laser light scattering application

Dana Castro, danamichelecastro@gmail.com. Brookhaven Instruments, Holtsville, New York, United States

When an aqueous solution has a certain amount of surfactant molecules, micelles are formed. The hydrophilic heads of the surfactant molecules orient themselves toward the water molecules while the hydrophobic tails orient towards each other, avoiding contact with water. These spherical aggregates are widely used in drug delivery, cosmetics, water treatment, detergents, and more. Characterization of these molecules can help qualify their performance. One common way of characterizing solutions like these is using non-invasive laser light scattering. This technique can be used to measure particle size, charge, and rheological properties.

A popular facial cleanser on the cosmetic market right now is micellar water. Many

companies carry this product and tout its ability to remove dirt, oil, and makeup while not irritating skin. The main ingredients of the commercial cleanser are water, surfactant, and moisturizer; with fragrance often added. Currently, it is not clear whether a qualification or characterization method for these formulations has been established. The presence of micelles and the solution's dilute nature makes it a candidate for characterization by laser light scattering.

In order to determine if light scattering could be used to characterize commercial micellar waters, four different commercial brands and formulations were obtained. A fifth micellar water was made in the laboratory using the three main ingredients to serve as a control. All five solutions were measured by Dynamic Light Scattering (DLS) to obtain size information, Phase Analysis Light Scattering (PALS) to obtain zeta potential information, and microrheology to obtain complex viscosity information using a Brookhaven Instruments NanoBrook Omni. All formulations contained a major size population around 10 nm, while also containing larger populations up to the single micron range. Two formulations revealed a negative zeta potential while the remaining three were neutral. Microrheology results were nearly the same across all formulations. All of these results may provide insight into how additives behave and influence micellar behavior as well as the formulation's efficacy and stability.

Overall, this study was successful in demonstrating the effectiveness of light scattering as a way to characterize micellar water. Light scattering analysis could provide a simple and effective QC processing method and help improve formulations in the future.

COLL 252

Modeling of nanoparticle immersion and self-assembly at liquid-air interfaces

Tadeusz T. Nitka, ttnitka@msn.com, Lela Vukovic. Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas, United States

Advanced experimental approaches allow a controlled synthesis of monodisperse colloidal nanoparticles (NPs) with a variety of compositions (cores, ligands), sizes, and shapes. These NPs have been reproducibly assembled into a rich spectrum of superstructures with characteristics different from bulk systems. Many types of superstructures have been prepared in bulk solutions. Recently, ultrathin films of nanoparticles have been prepared at interfaces of immiscible liquids, where the assembly conditions and the obtained structures are rather different. To investigate the behavior of NPs at the liquid-liquid and liquid-air interfaces, we performed precise atomistic molecular dynamics (MD) simulations of a variety of NPs at representative interfaces. Both NP shapes and ligand-solvent interactions were revealed to have an effect on the immersion and orientation of NPs at the solvent-air interface. The positioning of NPs at these interfaces influences their self-assembly, and could lead to self-assembly of previously unknown superlattices.

COLL 253

Multicolored protein colloidal particles: Rational methods to enhance their photostabilities

Melissa Limbacher, melissa.limbacher@uconn.edu, Bobbi S. Stromer, Julia Waldman, Challa V. Kumar. Univ of Connecticut, Storrs Mansfield, Connecticut, United States

Bovine serum albumin was cross-linked under controlled conditions to form protein colloidal nanoparticles, and particle size has been controlled from 20 to 100 ± 10 nm by choosing appropriate reaction conditions. The particles are then labeled with a small set of fluorescent dyes and the absorption as well as the emission wavelengths of the colloids (GlowDots) are controlled without changing the particle size, unlike quantum dots. GlowDots are convenient for cellular imaging and therefore, we examined their photochemical stabilities under defined sets of conditions. For example, GlowDots that have peak absorption wavelengths at 494, 543, and 576 had sufficient stabilities and irradiation of the particles at their peak absorption wavelengths over 30 minutes indicated only 10% loss. Thus, the particles have low photobleaching quantum yields (<0.1). Photoirradiation of the protein with these dyes, before the particle synthesis, followed by particle formation markedly enhanced the photostability of the particles. Thus, a rational approach is designed to increase the already high photostabilities of these protein colloidal particles even further.

COLL 254

Multigram synthesis of Cu-Ag nanowires and its application in 3D printing

Mutya A. Cruz, mutya.cruz@duke.edu, Benjamin J. Wiley. Chemistry, Duke University, Durham, North Carolina, United States

Printed electronics enable the production of devices with unconventional geometries or mechanical properties, such as flexible, stretchable, and wearable electronics. Within the last several years, 3D printing has been increasingly applied to printed electronics due to its advantages in producing electronics with complex geometries that improve functionality but are too costly or complicated for traditional fabrication techniques. It also enables rapid prototyping, which reduces the time spent designing devices. To accomplish this, specialized inks or filaments are necessary to add functionality to the printed object. Thus, there is a need for a highly conductive 3D printing material that is compatible with consumer-grade tabletop 3D printers, which eliminates the need for expensive inks and printers that are often used with this technique.

This poster presents the development of a conductive polymer composite filament containing Ag-coated Cu nanowires. Due to the high aspect ratio of the nanowires, a conductive network could be formed at low volume fractions. However, even a small batch of 3D printing filament requires tens of grams of nanowires. Production of this filament was enabled by the development of a relatively green and fast multigram

synthesis of Cu nanowires (4.4 g in 1 hr), and a method to coat the nanowires with Ag within 1 hr. The Cu nanowires were coated with a ~3 nm Ag shell to protect them from oxidation at elevated temperatures and humid conditions, and due to the relatively large diameters of Cu nanowires (~240 nm) produced by this synthesis, a Ag:Cu mol ratio of 0.04 was sufficient. The resulting nanowire-based filament is the first of its kind and has a resistivity of 0.002 Ω cm, >100 times more conductive than commercially-available graphene-based 3D printing filaments. Composite containing 5 vol% of 50-mm-long Cu-Ag nanowires was more conductive than composites containing 22 vol% of 20-mm-long Ag nanowires or 10-mm-wide flakes, indicating that high-aspect ratio Cu-Ag nanowires enable the production of highly conductive composites at relatively low volume fractions. The highly conductive filament can support current densities between 2.5–4.5 $\times 10^5$ A m^{-2} depending on the surface-to-volume ratio of the printed trace, and enables the 3D printing of a conductive coil for wireless power transfer.

COLL 255

Multimicrometer noncovalent monolayer domains on layered materials through thermally controlled Langmuir–Schaefer conversion for noncovalent 2D functionalization

Tyler R. Hayes⁴, hayes110@purdue.edu, Jae Jin Bang¹, Tyson C. Davis¹, Caroline F. Peterson¹, David G. McMillan², Shelley A. Claridge³. (1) Chemistry, Purdue University, West Lafayette, Indiana, United States (2) Bechtel Innovation Design Center, Purdue University, West Lafayette, Indiana, United States (3) Chemistry and Biomedical Engineering, Purdue University, Lafayette, Indiana, United States (4) Chemistry, Purdue University, Lafayette, Indiana, United States

Surface chemistry of 2D materials is often tailored through noncovalent functionalization strategies to avoid disrupting the electronic structure within the layered 2D material. Obtaining large-area structural control of noncovalently adsorbed molecular films for enhanced monolayer robustness is crucial in the design of novel hybrid materials and devices. Often during the fabrication process, noncovalently functionalized 2D materials are subjected to rigorous solution processing protocols. Langmuir-Schaefer protocols can be used to convert standing phases of amphiphiles on water into horizontally oriented monolayers on 2D materials, with varying degrees of molecular ordering and domain lengths of 100-1000 nm. Here we design and employ a custom-built temperature-controlled stage that enables *in situ* thermal annealing **during** Langmuir-Schaefer conversion, routinely transferring domains with edge lengths >10 microns. Monolayers with large highly-ordered polymerized domains were more stable towards vigorous washing with polar and nonpolar solvents. This method suggests utility for large-area structural control in noncovalently functionalizing 2D materials requiring solution processing as part of device fabrication.

COLL 256

Multi-stimuli responsive Pickering emulsion based on coumarin surfactants and silica nanoparticles

Yu Shijie, 18861822890@163.com, Jianzhong Jiang, Zhenggang Cui. Jiangnan University, Wuxi, Jiangsu Province, China

A dual stimuli-responsive Pickering emulsion with CO₂/N₂ and light triggers is prepared using negatively charged silica nanoparticles in combination with a trace amount of coumarin surfactant, 7-((10-(dimethylamino)-decyl)-oxy)-coumarin (7-OAC), as stabilizers. The molecule of 7-OAC contains both a charged amine group and a coumarin group, which are CO₂/N₂-sensitive and photoactive, respectively. On one hand, the emulsion can be transformed between stable and unstable rapidly via the N₂/CO₂ trigger, and on the other hand, a change in droplet size of the emulsion can occur upon light irradiation/rehomogenization cycles without changing the particle/surfactant concentration. The dual responsiveness thus allows for a precise control of emulsion properties. Since CO₂/N₂ and UV light are both low cost, environmentally benign and free of contamination, the Pickering emulsions may have potential applications in biomedicine, microfluidics, and drug delivery.

COLL 257

Multi-stimuli responsive wormlike micelles based on conventional surfactants

Qianqian Xu, 1037602596@qq.com, Jianzhong Jiang, Zhenggang Cui. Jiangnan University, Wuxi, Jiangsu Province, China

Stimulus-responsive surfactant wormlike micelles have been widely investigated in the past decade. Here, a triple-stimuli (pH-, thermo-, and redox reaction responsive) wormlike micelles was constructed with cetyltrimethylammonium bromide (CTAB) and 2,2'-Dithiosalicylic acid (DTSA). The system was fast and reversibly responded to pH-, thermo-, and redox reaction stimuli and it showed a circulatory gel/sol transition. Moreover, these transitions were switchable at least three times. The corresponding responsive behaviors of wormlike micelles were revealed using rheometer, cryogenic transmission electron microscopy, and ¹H NMR. The multi-stimuli responsiveness of the solution allowed for precise control of the wormlike micelles, and these micelles will have a wide range of applications in the development of functional materials for pharmaceutical or biomedical materials.

COLL 258

Nanofibrous scaffolds produced by electrospinning, rotary-jet spinning and airbrush for orthopedic tissue regeneration

Paria Ghannadian¹, *ghannadian.p@husky.neu.edu*, **James W. Moxley**¹, **Mirian De Paula**², **Thomas J. Webster**¹. (1) *Chemical Engineering Department, Northeastern University, Boston, Massachusetts, United States* (2) *Universidade do Vale do Paraíba, Sao Paulo, Brazil*

Recently, scientists have been investigating novel materials and techniques to meet growing orthopedic tissue engineering needs. Due to problems (such as infection and long healing time) that titanium based implants cause in vivo, new polymeric materials have been introduced. Polycaprolactone (PCL) is a bioresorbable and biocompatible polymer with potential applications for bone and cartilage repair. In this study, polycaprolactone fibers (with and without hydroxyapatite nano particles (nHAp) and carbon nanotubes (CNT)) were produced using three different methods: electrospinning, rotary-jet spinning and airbrush. The scaffolds were characterized using contact angles, differential scanning calorimetry, scanning electron microscopy, and were subjected to cell culture, bacterial assays, and mechanical (tensile) testing. The biological and material properties were studied to understand how the various fabrication techniques and nanoparticles affect human osteoblasts, gram positive (*Staphylococcus Aureus*) and gram negative (*Pseudomonas aeruginosa*) bacteria growth on samples. Experiments showed no toxic effect on osteoblast cells and a significant decrease in bacterial density by adding nHAp and CNT to the PCL scaffolds without using growth factors or antibiotics. Most importantly, results showed that without the use of antibiotics, by only changing the fabrication method and the size of the fibers, antimicrobial properties were improved without sacrificing mechanical properties and osteoblast functions. Among the different fabrication methods, airbrushed fibers indicated the highest elastic modulus compared to the other two techniques. Specifically, it was found that the antimicrobial properties were improved when using airbrushing compared to electrospun and rotary-jet spun scaffolds, where up to a 50% decrease in bacterial density was observed. To assess osteoblast biocompatibility and differentiation, cell proliferation, viability, adhesion, and calcium deposition assays were conducted. Although the cell proliferation, calcium deposition and cell viability results are similar, it is observed that the cell adhesion in airbrushed samples are poorer than those in electrospun and rotary-jet spun scaffolds.

COLL 259

Nanogels of hyaluronic acid bi-modified with epigallocatechin-3-gallate and curcumin: Potent nano-inhibitor on amyloid β -protein aggregation and cytotoxicity

Zhiqiang Jiang, **Xiaoyan Dong**, *d_xy@tju.edu.cn*, **Yan Sun**. *Department of Biochemical Engineering, Tianjin University, Tianjin, China*

Inhibition of amyloid β -protein (A β) aggregation is considered as a promising strategy for the prevention and treatment of Alzheimer's disease. Epigallocatechin-3-gallate (EGCG) and curcumin have been recognized as effective inhibitors of A β aggregation. Herein, we proposed dual-inhibitor modification of hyaluronic acid (HA) to explore the

synergistic effect of the two inhibitors. EGCG-modified HA (EHA) formed dispersed hydrogel structures, while EGCG-curcumin bi-modified HA (CEHA) self-assembled into nanogels like curcumin-modified HA (CHA). Thioflavin T fluorescent assays revealed that the inhibitory effect of CEHA was 69% and 55% higher than EHA and CHA, respectively, and cytotoxicity assays showed that the viability of SH-SY5Y cells incubated with A β and CEHA was 28% higher than that with A β and the mixture of EHA and CHA. These results clearly indicate the synergism of the two inhibitors. It is considered that the difference in the hydrophobicities of the two inhibitors made the bi-modification of HA provide a favorable CEHA nanostructure that coordinated different inhibition effects of the two inhibitors. This research indicates that fabrication of dual-inhibitor nanosystem is promising for the development of potent agents against A β aggregation and cytotoxicity.

COLL 260

Nanozymes for controlling localization and kinetics of bio-orthogonal reactions

*Riddha Das*¹, *das.riddha@gmail.com*, *Gulen Y. Tonga*², *Ryan F. Landis*³, *Prem Sak Puangploy*¹, *Michael Knapp*⁴, *Vincent M. Rotello*⁵. (1) *UMass Amherst, Amherst, Massachusetts, United States* (2) *Harvard University, Boston, Massachusetts, United States* (4) *Department of Chemistry, UMass at Amherst, Amherst, Massachusetts, United States* (5) *Univ of Massachusetts, Amherst, Massachusetts, United States*

Transition metal catalysts (TMCs) can catalyze a wide variety of chemical transformations, making them potential tools for bioorthogonal catalysis. We recently demonstrated that TMCs can be encapsulated in the surface monolayer of nanoparticles (NP), generating water-soluble “nanozymes”. These nanozymes demonstrate catalysis reminiscent of enzymes but can also catalyze a variety of bioorthogonal processes. Most studies of enzymatic activity have focused mainly on efficient catalysis rather than creating a modular system with selective and tunable catalysis. Here, we report a rational approach to control catalysis of nanozymes by fine-tuning their surface chemistry. These nanozymes possess different surface functionality to regulate their interaction with a library of profluorophore substrates. We determined that nanozyme catalysis efficiency was driven by supramolecular interactions between the nanozymes and substrates. This observation was validated by varying the hydrophobicity of both the nanozymes and substrates simultaneously. This fundamental study of nanozyme-substrate interactions provides the nanozymes with tunable catalysis reminiscent of their enzyme prototypes.

COLL 261

New approach of synthesizing anisotropic iron oxide nanoparticles with enhanced T₂ relaxation for MRI applications

*Sameera Wickramasinghe*¹, *smw151@case.edu*, *Shu F. Situ*¹, *Eric C. Abenojar*¹, *Bernadette O. Erokwu*², *Chris A. Flask*^{2,3}, *Zhenghong Lee*², *Anna C. Samia*¹. (1)

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, United States (2) Department of Radiology, Case Western Reserve University, Cleveland, Ohio, United States (3) Department of Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio, United States

Biocompatible iron oxide nanoparticles (IONPs) with high spin-spin relaxivity are ideal T_2 contrast agents for magnetic resonance imaging (MRI) applications. So far, IONPs with improved magnetic properties and enhanced T_2 relaxation have been achieved by either doping heteroatoms to the crystal lattice or inducing morphological changes via ion-directed or oxidative etching approaches. Furthermore, theoretical studies have shown that anisotropic IONPs are great candidates as T_2 contrast agents compared to their symmetric counterparts with similar dimensions, due to increased effective radius of the local magnetic field associated with anisotropic IONPs. In this study, we introduce a new approach of synthesizing anisotropic IONPs with concave cubic shape in the presence of a bulky coordinating solvent, trioctylamine, during the thermal decomposition of an iron-oleate metal precursor as opposed to traditionally used non-coordinating solvents, which generally produce spherical IONPs. We were able to demonstrate that the as-prepared concave IONPs have high T_2 relaxivity ($862.2 \text{ mM}^{-1} \text{ s}^{-1}$), and a 2-fold enhancement in T_2^* -weighted *in vivo* MRI contrast compared to spherical IONPs.

COLL 262

New nanocomposites of silicon polymers and noble metal nanoparticles for applications in 3D printing

Bhanu P. Chauhan¹, *chauhan.cepm@gmail.com*, **Natasha Ampomah**², **Kelly Moran**¹, **Qiaxian Johnson**¹. (1) Department of Chemistry, William Patterson University, Wayne, New Jersey, United States (2) Department of Chemistry, William Paterson University, Wayne, New Jersey, United States

In recent years our laboratory has been investigating the polymerization of bi-functional silane such as n-(2-aminoethyl)-3aminosilanetriol (2-AST) for creating materials for new technological applications. In this work our goal is to create a new hybrid polymer system which have a varied amount of metal nanoparticles nucleated within them. We are investigating such materials for their real life applications in the fields such as 3D printing. In these systems, we are exploiting the characteristic properties of hybrid polymers as nano-sized building blocks to create devices with tiny features that are otherwise inaccessible we plan to create inexpensive methods to prepare solar cells, catalysts support, strong fibers, and medical devices. Our methodology pivots on simplicity of our approach, inexpensive starting materials and high end utility of the products.

Sonochemistry is well used in industry for emulsifying, catalyzing and various other applications to its high throughput and quick reaction rates. In this presentation, we will disclose the sonication of bi-functionally stabilized gold and silver nanoparticles (AuNP's/AgNP's), and Si-H containing well defined polymers such as PMHS to produce

nanocomposites of unique characteristics. In this process, the cross-linking and polymerization is accomplished at room temperature under ambient conditions. We were able to create heterogeneous fibers containing evenly distributed metal nanoparticles. We will also present their applications in 3D printing. In 3D printing applications, we used copolymer of acrylonitrile butadiene styrene (ABS) with our nanocomposites. We will present our results of these studies and the detailed characterization of new products using NMR, TEM, SEM, FT-IR, Raman, TGA, and UV-Vis techniques as well as the 3D objects made from our materials for applications in catalysis.

COLL 263

Nitrogen-doped graphene quantum dots / TiO₂ composite for photocatalysis

Reece Lawrence, reece.lawrence@mail.utoronto.ca, M. Cynthia Goh. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

Nitrogen-doped graphene quantum dots (NGQD) and TiO₂ composite structures were synthesized via hydrothermal reaction. The composite structure is characterized through a variety of techniques including X-Ray Diffraction (XRD) and High Resolution Transmission Electron Microscopy (HR-TEM). Sub-10 nm anatase TiO₂ nanoparticles were covalently bonded with NGQDs to form a strong electronic coupling that facilitates the photogenerated charge transfer and separation at the NGQD/TiO₂ interface. By monitoring the photocatalytic degradation of Rhodamine B, it was found that the photocatalytic performance of optimized NGQDs/TiO₂ composite is over 5 times higher than that of regular TiO₂ nanoparticles.

COLL 264

Novel synthetic method of chitosan functionalized liposomes as an innovative nanocarrier for chemotherapeutic drugs

Lindsey Hyppolite, lindseyhyppolite7110@comcast.net. Chemistry, Delaware State University, Dover, Delaware, United States

Liposomal nanoparticles are essential in the delivery of chemotherapeutic drugs in the treatment of multiple myeloma cancer. The development of an ideal liposomal nanoparticle drug delivery system is of increasing interest to ensure that the conjugated drug carrier complex arrives and acts preferentially at the tumor site with high efficacy and lower toxicity. The focus of this work lies in the microwave-assisted synthesis of functionalized liposomal nanoparticle with the biopolymer chitosan (CS) to enhance the stability and bio adhesivity of the liposomal nanoparticle system. Characterization of the liposome vehicles were studied using Fourier Transform Infrared Spectroscopy (FTIR), zeta potential analysis, particle size analysis (PSA), and scanning electron microscopy (SEM). Preliminary findings in the characterization of the synthesized liposomes using FTIR showed characteristic symmetric and antisymmetric CH₂ (at 2,800–3,000 cm⁻¹)

bands and the C=O (at $1,740\text{ cm}^{-1}$) stretching bands attributed to the presence of chitosan on the liposome surface. Structural characteristics of the synthesized liposomes were also studied by dynamic light scattering. The liposome suspensions presented exhibited mean diameters between 150 nm and 250 nm, polydispersity indexes (PDI) around 0.4, zeta potential values between -40 mV and -30 mV, indicating complex formation between the anionic liposomes and cationic chitosan molecules. The surface morphology of the scaffolds were studied using Scanning electron microscopy showed (SEM) and it was observed that the liposomes are uniform in diameter ($\sim 190\text{nm}$) with unilamellar structures. XRD analysis exhibited diffraction peaks corresponding to chitosan functionalization occurring at 20° . Stability studies of the functionalized CS-liposomes showed increased stability to aggregation than pristine liposomes when stored at ambient temperatures. The development of chitosan functionalized liposomal nanoparticle drug delivery systems (DDS) shows great promise in the delivery of anticancer drugs, through the reduction/elimination of toxic and adverse effects resulting from their administration.

COLL 265

On the shuttling mechanism of a chlorine atom in a chloroaluminum phthalocyanine based molecular switch

Huanjun Song, **Hao Zhu**, 1701110426@pku.edu.cn, Kai Wu. College of Chemistry Molecular Eng, Peking University, Beijing, China

An intermediate shuttling structure of a chloroaluminum phthalocyanine(CIAIPc)-based molecular switch is transiently created and analyzed by combined scanning tunneling microscopy/spectroscopy and density-functional theory calculations, which suggests that the Cl atom is squeezed into the space between the central Al atom and the inner N-containing ring in CIAIPc.

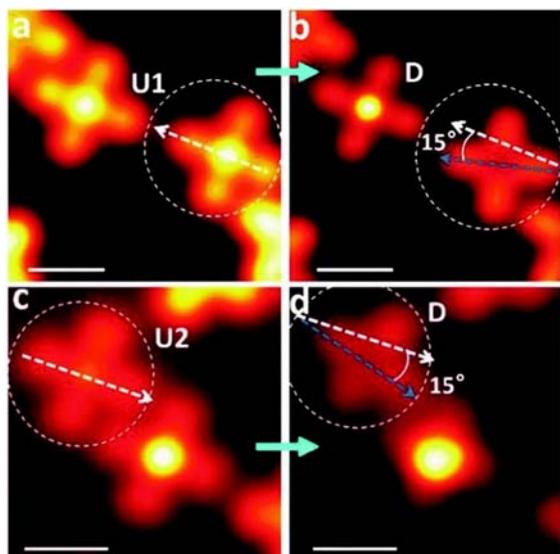


Fig. 1 STM images (a) before and (b) after Cl shuttling of the U1 molecule by applying a tip pulse of 2.9 V sample bias, yielding the D molecule. STM images (c) before and (d) after Cl shuttling of the U2 molecule by applying a tip pulse of 2.9 V sample bias, yielding the D molecule.

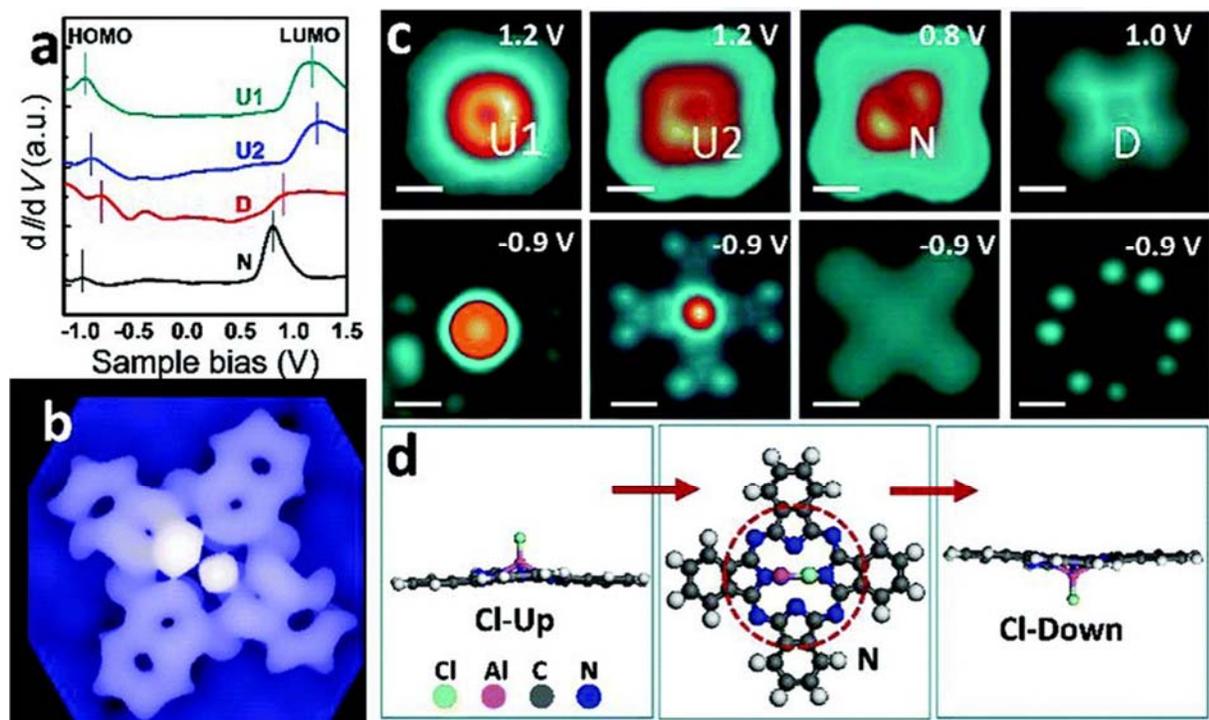


Fig. 2 (a) STS spectra with the LUMO and the HOMO highlighted of U1, U2, D and N molecules at the surface. (b) DFT simulated STM image of the N molecule. (c) dI/dV mappings of the U1, U2, D and N molecules. (d) Schematic drawing of the consecutive shuttling process of the Cl atom through the inner ring of the ClAlPc molecule.

COLL 266

Organic solvent dispersion of two-dimensional titanium carbide by the surface functionalization

Daesin Kim^{1,3}, Chong Min Koo^{1,3}, **Sangho Cho**^{1,2}, scho@kist.re.kr. (1) Korea Institute of Science and Technology, Seoul, Korea (the Republic of) (2) Division of Nano & Information Technology, Korea University of Science and Technology, Seoul, Korea (the Republic of) (3) KU-KIST Graduate School of Conversion Science and Technology, Korea University, Seoul, Korea (the Republic of)

As one of the newest family of 2D materials, 2D transition metal carbides and nitrides (MXenes) have attracted attention in a wide range of applications including energy storage, electromagnetic interference shielding, electrode, water purification, catalysis. The surface groups of -OH, =O, -F enable MXene well-dispersed in aqueous solution.

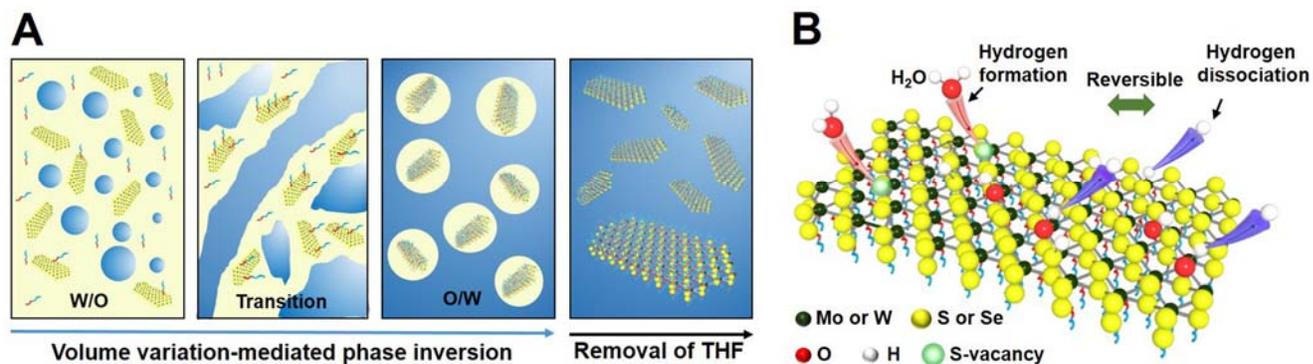
However, their dispersibility in organic solvents is limited in polar ones, such as ethanol, dimethylsulfoxide, N, N-dimethylformamide. Here, the study on surface modification of 2D transition metal carbide, T_3C_2Tx , is described. Also, the dispersibility of the resulting MXene nanoparticles in the various organic solvents is studied. The organic phase dispersion of nanoparticles would widen the compatibility of the nanoparticle with various media and polymer matrices, which can accelerate the research in functional materials.

COLL 267

Outstanding radical scavenging of transition metal dichalcogenide nanosheets via defect-mediated one-step hydrogen atom transfer in aqueous media

Ji Eun Kim¹, kgova@hanmail.net, Jin Yong Lee¹, Sung Jun Hong¹, Jin Woong Kim^{1,2}. (1) Bionano technology, Hanyang University, Ansan, Korea (the Republic of) (2) Chemical and Molecular Engineering, Hanyang University, Ansan, Korea (the Republic of)

Transition metal dichalcogenides (TMDs) have recently received a lot of attention because they exhibit thickness- and composition-dependent properties. In particular, TMDs have direct band gaps when bulk TMDs with indirect band gaps reach monolayers, resulting in intriguing chemical, electrical, and optical properties. One noteworthy feature of the TMD nanosheets from the structural point of view is that they can possess chalcogen defects that are known to be active sites. An oxidation-reduction process, which occurs in radical scavenging, can also be influenced by these reactive sites, and its designated energy barrier can be provided by the adjacent atoms across the surface of the TMD nanosheets, which can play a decisive role in enhancing the radical scavenging ability. Herein, we introduce a TMD-based antioxidation platform having excellent radical scavenging performance as well as structural stability under harsh storage conditions. The key to this approach is to fabricate a stable suspension of TMD nanosheets with an ultrathin platelet configuration that exhibits the defect-mediated one-step hydrogen atom transfer. Accordingly, we fabricated the stable suspension of TMD nanosheets by enveloping them with a monolayer of an amphiphilic diblock copolymer, poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO). We subsequently characterized the optical and structural properties of PCL-*b*-PEO-enveloped TMD nanosheets. Finally, we demonstrated that the TMD nanosheets fabricated in our study showed outstanding radical scavenging activities in aqueous media by using ABTS assay (2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) under a variety of storage conditions. These characteristics highlight that the TMD nanosheets fabricated in this study can be used as promising radical scavengers, encouraging the further investigation of these functional TMD materials for biological applications.



(A) Schematic illustration of the fabrication of PCL-*b*-PEO-enveloped TMD nanosheets by phase inversion. (B) Schematic illustration of the defect-mediated one-step hydrogen atom transfer on a TMD nanosheet in aqueous medium.

COLL 268

Pegylation of β -cyclodextrin for increased water solubility and biocompatibility in drug delivery applications

Kim T. Nguyen, **Roni Manasi**, Ronim3210@yahoo.com, **Larry Rodriguez**, Irodr146@calstatela.edu, Yong Ba. Chemistry, California State University Los Angeles, Glendale, California, United States

Cyclodextrins (CDs) are cyclic oligosaccharides that are (1, 4) linked α -D(+)-glucopyranose units. CDs have a truncated cone-like shape with a relatively hydrophobic inner cavity and a hydrophilic exterior. Thus, CDs have been widely used as drug delivery carriers. β -CD contains 7-D(+)-glucopyranoside units, and is the most commonly used CD in the pharmaceutical industry. However, β -CD's drawbacks lie in its low water solubility due to the intramolecular hydrogen bonds among the secondary hydroxyl groups on the peripheries, and the nephrotoxicity for drug delivery through parenteral administration. To tackle these adverse effects, we have attached poly(ethylene glycol) methyl ether (mPEG) to β -CD's exterior region to render β -CD the properties of water solubility and biocompatibility. The synthesis of the pegylated β -CDs was carried out by tosylating the mPEG, de-protonating the hydroxyl groups on the β -CD to form strong nucleophiles, and combining them together through an S_N2 mechanism to obtain the target compound, mPEG- β -CD. ¹H 2D COSY and NOESY NMR, and MALDI-TOF mass spectrometry techniques were used to characterize the structures and molecular weights of the products. We found that solubility of the pegylated β -CDs was significantly improved. 1-fluoroadamantane, a model drug, was used to examine the inclusion property of the pegylated β -CD. The results show that the cavities of pegylated β -CDs were still open and available for drug loading. The increased water solubility and drug loading capabilities of pegylated β -CDs combined with PEG's biomedical properties predict the promise of pegylated β -CDs' applications in the pharmaceutical industry.

COLL 269

Photoinduced metallic particle growth on single crystal relaxor ferroelectric strontium barium niobate

*Eftihia Barnes*¹, efthiabarnes@gmail.com, *Erik Alberts*², *L. C. Mimum*³, *Jonathon Brame*⁴, *Chris Warner*⁵, *Ashley R. Harmon*³, *Aimee R. Poda*⁶. (1) Geotechnical and Structures Laboratory, US Army Engineer Research and Development Center, Vicksburg, Mississippi, United States (2) HX5 LLC, Vicksburg, Mississippi, United States (3) Environmental Laboratory, US Army Engineer Research and Development Center, Vicksburg, Mississippi, United States

The photochemical growth of metallic particles on the surface of single crystal relaxor ferroelectric strontium barium niobate ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ or SBN:100x) is reported here. Silver and gold particles were deposited on unpoled (001) and (100) surfaces of SBN:61 by reduction of silver nitrate and gold chloride solutions under UV illumination. Wavelength-dependent experiments reveal that differences in the particle deposition pattern on the (001) and (100) surfaces can be primarily attributed to the anisotropic optical absorption of SBN. Particle deposition on electric field poled (001) SBN:60 show enhanced particle deposition on positive domains, and suppressed deposition on negative domains, with unusual deposition patterns observed on the perimeter of domains obtained from incomplete switching. Based on our experimental observations, we propose a band diagram for the SBN/solution interface and discuss mechanisms influencing particle deposition. Further, we investigate the effect of the deposited metallic particles on the wettability of the SBN surface and the realization of surface enhanced Raman spectroscopy (SERS).

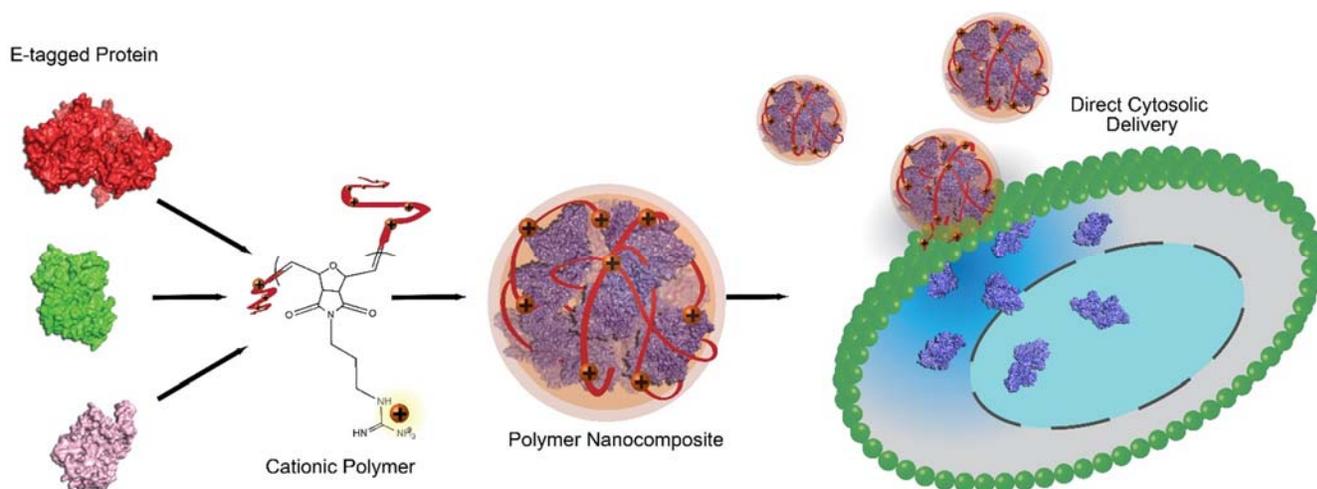
COLL 270

Polymeric nanoassemblies for direct delivery of active therapeutic proteins

*David C. Luther*¹, dcluther28@gmail.com, *Yi-Wei Lee*², *Federica Scaletti*², *Ryan Landis*², *Vanessa D. Chaplin*², *Michael Mingroni*², *Li-Sheng Wang*², *Moumita Ray*³, *Rubul Mout*^{4,3}, *Vincent M. Rotello*⁵. (1) Chemistry, University of Massachusetts, Amherst, Massachusetts, United States (2) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (3) Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States (4) Institute for Protein Design, University of Washington, Seattle, Washington, United States (5) Univ of Massachusetts, Amherst, Massachusetts, United States

The field of protein therapeutics offers significant clinical promise, but lacks a simple platform for cytosolic delivery of bioactive proteins. Here, we describe a generalized method for the direct delivery of therapeutic proteins in their active form into the cytosol of the cell via a biodegradable, non-immunogenic delivery platform. This is accomplished using a functionalized cationic poly oxanorbornene imide (PONI) polymer, and an engineered glutamic acid-tagged (E-tagged) variant of the protein of interest.

These polymer nanocomposites fuse with the cell membrane to deliver their protein cargo directly into the cytosol, without suffering from entrapment or degradation. This system was implemented using three proteins of varying size, charge, and function to demonstrate its versatility. This wide range of potential demonstrates the feasibility of this platform for the effective, generalized delivery of therapeutic proteins.



COLL 271

Polymeric pH-activated nanoparticles for lipo-toxic cell application

Kaitlynn Lopes¹, kmlopes@bu.edu, **Jialiu Zeng**², **Mark W. Grinstaff**^{3,2}. (1) Chemistry, Boston University, Boston, Massachusetts, United States (2) Biomedical Engineering, Boston University, Boston, Massachusetts, United States (3) Boston Univ Dept of Chem, Boston, Massachusetts, United States

Non-alcoholic fatty acid liver disease (NAFLD) affects between 20-30% of the Western adult population. NAFLD is characterized by cellular lipotoxicity caused by an overexposure of free fatty acids (FFAs) to cells. Excess FFAs causes increased lysosomal pH and inhibition of autophagic processes crucial to maintaining normal cellular function. We propose the development of polymeric pH-activated nanoparticles for acid delivery to the lysosomes within lipo-toxic liver cells for the promotion of autophagy and restoration of the internal cellular environment. Nanoparticles were synthesized from the polymer, poly (butylene tetrafluorosuccinate-co-succinate) ester, which is composed of varying ratios of tetrafluorosuccinic acid to succinic acid and butylene glycol. Nanoprecipitation was used to form the nanoparticles, and different factors including the solvent type, the surfactant type, the polymer to surfactant ratio concentration, temperature, duration of dialysis, and the polymer type were varied to determine the optimized conditions for nanoparticle formation. Proper nanoparticle synthesis was confirmed using Dynamic Light Scattering, Zeta Potentializer, and Scanning Electron Microscopy techniques to determine the average diameter, polydispersity, stability, and morphology of each nanoparticle formulation respectively.

Nanoparticles with an average diameter of approximately 100 nanometers and a polydispersity between 0.1 and 0.2 were deemed ideal for cellular uptake. Optimal nanoparticles were formed at room temperature with a 1:4 polymer to surfactant final concentration ratio, and a dialysis time of 24 hours using dimethylformamide as the solvent for polymer dissolution and sodium dodecyl sulfate (SDS) as the surfactant. The nanoparticles were determined to be non-cytotoxic and have the ability to modulate lysosomal pH.

COLL 272

Predominated thermodynamically controlled reactions for suppressing cross nucleations in formation of multinary substituted tetrahedrite nanocrystals

Suman Bera, *mssb6@iacs.res.in. Material Sciences, Indian Association for the Cultivation of Science, Kolkata, West Bengal, India*

Group I-II-V-VI semiconducting $\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13}$ ($\text{M} = \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Mn}^{\text{II}}$ and Cu^{II}) substituted tetrahedrites nanostructures remains a new class of multinary materials which have not been widely explored yet. Having different ions, the formation process of these nanostructures has always the possibility of formation of cross nucleations. Minimizing the reaction time, herein, a predominantly thermodynamically control approach is reported which decoupled the quaternary nucleations with their possible cross nucleations. As a consequence, possible cross nucleations were prevented and series of nearly monodisperse intriguing substituted tetrahedrite nanostructures are formed. The possible LaMer plot for this single- and also multi-materials nucleations is also proposed. Furthermore, bandgaps of all these new materials are calculated and preliminarily the applicability of these materials is tested for photoelectrochemical water splitting.

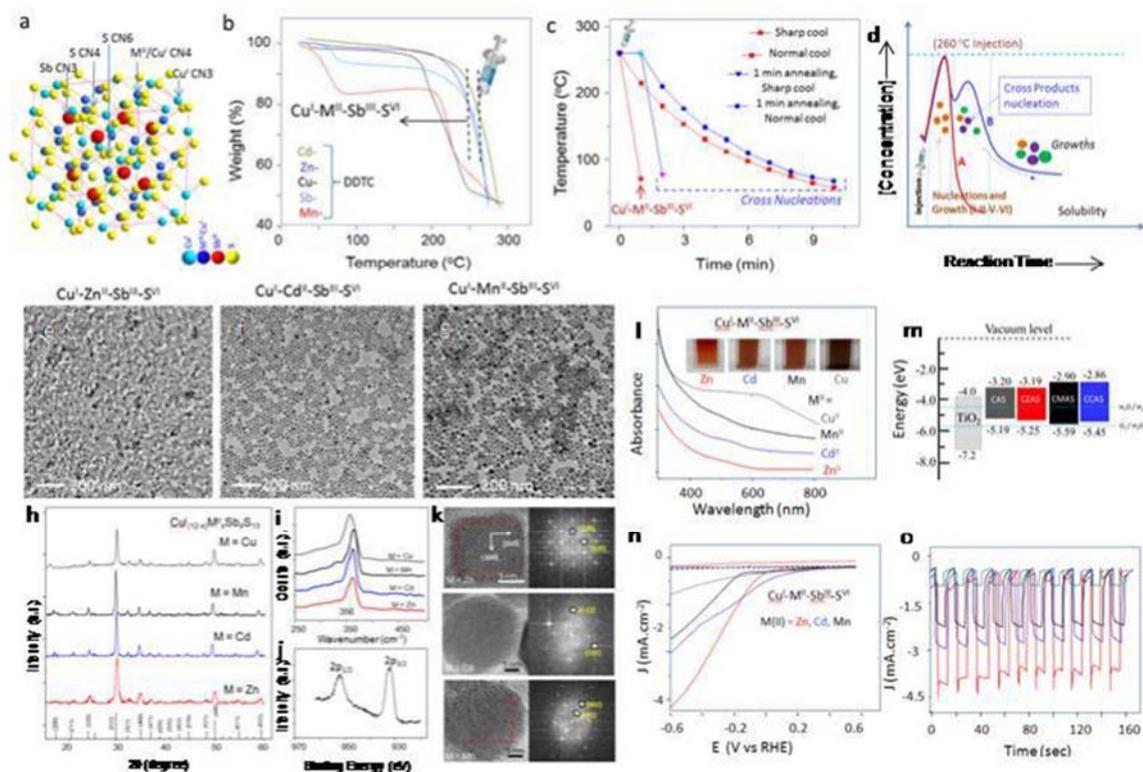


Figure 1. (a) Crystal structure of tetrahedrite crystal. (b) Thermogravimetric (TG) plots of DDTC complexes of Cu^{II} , Zn^{II} , Cd^{II} and Mn^{II} . (c) Reaction temperature vs. time plot. (d) Schematic presentation of LaMer plot. (e-g) TEM images of substituted tetrahedrites $\text{Cu}^{\text{I}}_{10}\text{M}^{\text{II}}_2\text{Sb}_4\text{S}_{13}$ nanocrystals where $\text{M}=\text{Zn}$, Cd and Mn respectively. (h) Powder XRD patterns. (i) Raman spectra. (j) X-ray photoelectron spectra of Cu in $\text{Cu}^{\text{I}}_{10}\text{M}^{\text{II}}_2\text{Sb}_4\text{S}_{13}$ ($\text{M}=\text{Zn}$). (k) HRTEM of single nanocrystal of these substituted nanocrystals and their selected area FFT patterns. (l) Absorption spectra of different tetrahedrites. (m) Band positions. (n) Linear cyclic voltamogram. (o) The time-dependent photocurrent density of different photocathodes at -0.5 V vs. SCE.

COLL 273

Preparation of flexible silver-colored organic crystals

Kazuki Yamada¹, tus4213096@gmail.com, **Yutaka Takahashi**², **Yukishige Kondo**¹. (1) Dept Ind Chem, Tokyo Univ SCI, Shinjuku, Tokyo, Japan (2) Industrial Chemistry, Tokyo University of Science, Tokyo, Japan

There are a number of materials and products exhibiting a metallic luster around us. These luster is brought about by real metals. Although metallic paints can form metal-lustrous film on solids, they contain fine metal particles. Therefore, painted films obtained from metallic paints are opaque to radio waves. Our research group has found that a stilbene (DC-stilbene) (**Fig. 1**) forms silver-lustrous crystals which are transparent to radio waves. However, the crystals are brittle and breakable. In this work, a novel

DC-stilbene derivative has been synthesized in order to improve the fragility of the previous silver-lustrous crystals.

New DC-stilbene derivative **1** has been synthesized through 4 reaction steps. Total yield was 28%.

After **1** was dissolved in the mixture of CHCl_3 and methanol on heating, the solution was put and cooled under a room temperature to obtain fine crystals. These crystals were recovered onto a filtration paper ($\varnothing = 21 \text{ mm}$) by filtration. The recovered crystals were silver-colored. Compared to the silver-colored crystals of DC-stilbene, those of **1** were flexible and foldable (**Fig. 2**). The crystals of **1** may have a potential as a silver-colored film or stick-on which is transparent to radio wave and applicable to not only flat surfaces but also curved surfaces.

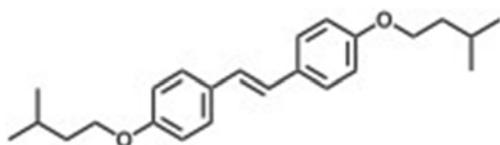


Fig. 1 Chemical structure of DC-stilbene

a) crystals of a previous stilbene derivative



b) Novel crystals of **1**



Fig. 2 Silver-colored crystals of DC-stilbene and **1**

a) DC-stilbene, b) New compound **1** (flexible and foldable)

COLL 274

Probe aggregation into the interfaces between mimicking raft and non-raft domains, induced by peptide nucleic acid (PNA) duplexes

Yoshimi Oka, oka-yoshimi@oita-u.ac.jp. Research Promotion Institute, Oita University, Oita, Japan

Cell membranes are known to exhibit non-uniform distribution of lipids and cholesterol, i.e., to form microdomain structures (lipid rafts) that serve as platforms for specific

recruitment of proteins related to transportation and signal transduction. I focus on the reaction field such as lipid rafts to increase concentration of substrates. Recently, we demonstrated that a new flavin probe, composed of palmitoylated peptide nucleic acid (PNA) and its complementary PNA labeled with flavin, targets the liquid-ordered (lo) microdomains (i.e, mimicking rafts) and disrupts its interfaces to liquid-disordered (ld) microdomains of giant unilamellar vesicles (GUVs), and can be visualized by using confocal laser scanning microscopy. Surprisingly, the probe disrupted lo–ld interfaces as observed in the time-lapse images, in which vesiculations and aggregations of both probes, labeled PNA duplex and Texas Red–1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine (TR–DHPE, almost exclusively partitioned into the ld domain) appeared. From the control experiments with labeled DNA instead of labeled PNA showing that the lo domains remained stable enough to assess quantitative fluorescence analysis. Accordingly, we interpreted the vesiculations and probe aggregations may be induced by redistribution of PNA duplex and its forming large curvatures in lo–ld interfaces. Further studies to concentrate some probes at the interfaces will be also presented.

COLL 275

Production of bimetallic nanoparticles in vapor phase

Naomi Sakono, *nsakono@nc-toyama.ac.jp*, Kazuki Omori, Koki Yamamoto. Department of Applied Chemistry, National Institute of Technology, Toyama College, Toyama, Japan

Bimetallic nanoparticles, composed of two metal elements in a single particle, exhibit interesting optical, chemical, and biological properties. Among the various structures of bimetallic nanoparticles, the core–shell structure is scientifically interesting, especially from the viewpoint of catalysis. Core–shell bimetallic nanoparticles have higher catalytic activity than monometallic ones. The compositions of the core and shell of bimetallic nanoparticles produced in liquid phase depends on the ionization tendency of the atoms. In this study, we have investigated the vapor-phase production of core–shell bimetallic nanoparticles, which is independent of the ionization tendency of nanoparticles.

Two furnaces were connected and then Ag and Au grains were placed in them. The Ag and Au grains loaded in a quartz tube were vaporized at around 1100 °C and 1500 °C in a furnace with N₂ gas flow under atmospheric conditions. The obtained nanoparticles were analyzed using transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, and UV-vis spectrophotometry. The TEM image shows that the diameter of the captured nanoparticles was under 10 nm. The EDX spectrum shows that the nanoparticles obtained had a homogeneous alloy structure. The UV-vis absorption spectrum shows that the wavelength of the plasmon resonance shifted compared with that of the Ag and Au nanoparticles. These results suggest that the produced nanoparticles were composed of Ag and Au. The details of the structure of the produced nanoparticles (whether or not composed of core–shell) will be discussed at the poster presentation.

COLL 276

Production of golden luster by mixing an azobenzene derivative with liquid crystals

Ko Fukushima¹, *fk.patopon.14@gmail.com*, **Yutaka Takahashi**², **Yukishige Kondo**¹. (1) *Dept Ind Chem, Tokyo Univ SCI, Shinjuku, Tokyo, Japan* (2) *Industrial Chemistry, Tokyo University of Science, Tokyo, Japan*

Our group has found that gold-lustrous organic crystals are obtained from an azobenzene derivative, bis[4-(3-methylbutoxy)phenyl]diazene (**DC-azo**), and reported that the golden luster results from the stack of a number of DC-azo monolayers in crystals. If **DC-azo** monolayers can be stacked in liquid crystals employing the ordered alignment of liquid crystal molecules, the obtained mixtures might show a golden luster. In this work, the production of golden luster by controlling molecular orientation of **DC-azo** using a thermotropic liquid crystal compound.

4-Cyano-4'-*n*-octylbiphenyl (8CB) has been used as a liquid crystal compound (crystal → liquid crystal: 21.5 °C; liquid crystal → isotropic liquid: 40.5 °C)

DC-azo and 8CB (1/0.8, mol/mol) were mixed on a slide glass, and heated above 126 °C which is the melting point of **DC-azo**. The obtained mixture turned to a red transparent liquid. When the mixture was put and cooled under a room temperature, it produced golden luster (**Fig.1**). However, **DC-azo** exhibited an orange color in the absence of 8CB. These results indicate that 8CB plays an important role in producing a golden luster of the **DC-azo**/8CB mixtures.



Fig.1 Gold-lustrous **DC-azo**/8CB mixture after cooling under a room temperature

COLL 277

Programmable DNA nanoparticle: Self-assembly of pH-triggered nucleic acid ion complex

Noriko Miyamoto, *n-miyamoto@aitech.ac.jp*, **Yukio Kitade**. *Aichi Institute of Technology, Toyota, Aichi, Japan*

DNA nanoparticle has attracted attention as a therapeutic oligo nucleotides delivery tool. There is a DNA nanostructure that can precisely control particle size and shape by using DNA nanotechnology. According to recent studies, tetrahedral DNA nanoparticle can

uptaking to immunocyte without being degraded by nuclease.

This research shows developing new concept of DNA nanoparticle with self-assembly of pH-triggered nucleic acid ion complex, using morpholino nucleotide (PMO) of chemically modified oligonucleotide (ODN). The conjugated DNA-(polyethylene glycol (PEG)) PEG and PMO-PEG formed double strand sequence at pH 7.4. At decreasing pH led to protonation of the PMO-PEG, resulting in aggregation of the ion complex. This aggregation was controlled by using sequence specific hydrogen bonding, charge interaction and conjugate-direction and molecular weight of PEG.

COLL 278

Protein-polymer colloids: 17-fold enhanced activities of cytochrome c conjugated with poly(acrylic acid)

Kyle R. Benson¹, kyle.benson@uconn.edu, Joseph Gorecki¹, Anton Nikiforov¹, Rajeswari Kasi², Yao Lin³, Challa V. Kumar². (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) University of Connecticut, Storrs Mansfield, Connecticut, United States (3) Inst of Materials Sci, University of Connecticut, Storrs Mansfield, Connecticut, United States

Protein-polymer colloids are of recent interest from fundamental point of view as well as due to their high promise for biological applications such as biocatalysis, imaging, cancer drug delivery. Here, we examined the peroxidase activities of cytochrome c-poly(acrylic acid) (cyt c-PAA) covalent conjugates where the molecular weight of PAA has been increased systematically. A linear relation between the enzymatic activity and molecular weight of the PAA was observed, and up to 17-fold enhancement in turnover number (k_{cat}) was noted. The colloids of cyt c-PAA were characterized by dynamic light scattering, electron microscopy and other biophysical methods. The effects of macromolecular crowding, substrate partitioning in the polymer phase, and PAA negative charge field on the kinetic enhancement were systematically studied. Taken together, these data indicated that polymer charge density and macromolecular crowding by the conjugated polymer could be adjusted to enhance the redox activity of cyt c. This concept was then extended to build colloids of horseradish peroxidase and hemoglobin, as well as enzyme-polymer films. Full biochemical and biophysical characterization will be presented.

COLL 279

QCM-D and spectroscopic study of cholesteric liquid crystals for temperature-responsive materials

Kathleen Swana¹, kathleen.w.swana.civ@mail.mil, Paola D'Angelo¹, Shani Levit², Ratib Stwodah², McKenna Gillard², Christina Tang². (1) Emerging Materials Development Team, NSRDEC, Natick, Massachusetts, United States (2) Chemical and Life Science Engineering, Virginia Commonwealth University, Richmond, Virginia, United States

This work addresses the objective of developing stimuli-responsive textile technologies containing cholesteric liquid crystals embedded within polymer matrices that will respond and adapt to changing environments. Multiple formulations of cholesteryl oleyl carbonate, cholesteryl pelargonate and cholesteryl benzoate were produced and their thermochromic behavior was characterized using polarized light microscopy, UV-Vis diffuse reflectance spectroscopy and quartz crystal microbalance with dissipation monitoring (QCM-D). Distinct shifts in peak reflectance of the liquid crystal formulations were observed between 400 nm and 750 nm, corresponding with temperature-induced color change. QCM-D was used to monitor molecular-scale changes in liquid crystal films as temperature increased in real-time. Incorporation of liquid crystals into polymer emulsions to produce polymer fibers through electrospinning was also explored and characterized. This knowledge will facilitate the future development of multifunctional temperature-responsive textiles.

COLL 280

Rapid and scalable synthesis of sub-10 nm metal nanoparticles in on-the-fly aerosols

Yong Yang¹, kyyoung@umd.edu, Pankaj Ghildiyal², Michael R. Zachariah^{1,2}. (1) Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland, United States (2) Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States

Metal nanoparticles incorporated in a host matrix like polymer or graphene have been widely used for a range of applications including energy storage, catalysis, and electronic devices. Manufacturing metal nanoparticles with high quality in an efficient manner, however, is still challenging due to their low stability and agglomeration tendency. This work investigates how growth and aggregation of these nanostructures can be circumvented by incorporating them into a matrix using an on-the-fly growth process. We demonstrate the formation of sub-10 nm particles of Ni, Co, Cu and Sn nanoparticles in both of polymer and graphene matrices using an aerosol single-drop reactor approach. The rapid thermal pulse given to the aerosol particles enables the formation of nuclei and growth, with subsequent rapid quenching to freeze in the structure. The role of reaction temperature and metal precursor loading on the formation of nanoparticles in the aerosols is discussed. A characteristic time analysis and an analysis of the particle size distributions lead to the conclusion that growth is governed by nucleation and surface growth, with little coagulation or Ostwald ripening. Finally, we note that this aerosol process offers considerable potential for the scalable synthesis of well-dispersed and uniform metal nanoparticles stabilized within the polymer/graphene matrix.

COLL 281

Role of slurry chemistry on the nanoparticle redox behavior relevant to the shallow trench isolation chemical mechanical planarization process

Tala Zubi, *talabzubi@lewisu.edu*, **Cynthia Saucedo**, *cynthiasaucedo@lewisu.edu*, *Katherine Wortman-Otto, Carolyn Graverson, Jason J. Keleher. Dept of Chem, Lewis University, Romeoville, Illinois, United States*

Isolating inert regions and active pathways within an integrated circuit (IC) is facilitated through dielectric deposition of tetraethyl orthosilicate (TEOS) during shallow trench isolation (STI). Chemical mechanical planarization (CMP) is used to selectively target and remove the excess TEOS overburden with colloidal suspensions (slurries) containing ceria (CeO_2) abrasives. Literature has shown that oxygen vacancies, indicating the presence of Ce^{3+} particles on the CeO_2 surface, are an important factor in achieving high material removal rates. A fundamental drawback of the reactive nature of Ce^{3+} is that it is more likely to remain on the polished surface, having the potential to induce defectivity via particle contamination and micro-scratches. To mitigate these defects, industrial methods such as standard clean 1 (SC-1) target the less reactive Ce^{4+} state to result in angstrom level uniformity using concentrated chemical agents. The focus of this work is to investigate the oxidation state of CeO_2 through UV-Vis and fluorescence spectroscopy. Results have shown a decrease in the ratio of $\text{Ce}^{4+}/\text{Ce}^{3+}$, which was tracked and correlated to increased removal rates in the presence of key slurry additives. Furthermore, understanding the interactions at the wafer interface are critical in unraveling the effect of the macromolecule and surfactant-based cleaning agents, which was studied using dynamic light scattering to monitor the particle size and zeta potential. Analogous to SC-1, the cleaning chemistry shows comparable particle removal using fluorescence microscopy; however at an increased efficiency, making it a viable alternative to traditional cleaning methods. Ultimately, both CMP and post-CMP processes have shown improvement through the understanding of the CeO_2 oxidation states, along with the particle encapsulated removal mechanism.

COLL 282

Seedless, one-pot synthesis of infrared-absorbing silver nanoparticles

Nobuyuki Yamamoto, *phdstudent2010@gmail.com*, *David P. Pullman. San Diego State University, San Diego, California, United States*

The optical properties of silver nanoparticles are well-known to depend on their size and shape, and for many applications, developing reproducible methods of synthesis is important. There are a number of reports in the literature describing methods of producing nanoparticles of controllable size and shape, which leads to UV-Visible absorption peaks that are tunable throughout the visible region; however, there are only a few that report maxima above 800 nm, and these generally use a seeded approach. In this study, we further develop the method of producing silver nanoparticles via the reduction of silver ions by sodium borohydride in the presence of sodium citrate and hydrogen peroxide. Through careful variation of reactant concentrations, mixing rates, and other reaction conditions, the UV-Visible absorption peaks can be tuned well into the near-infrared region. This approach is one-pot, seedless, and yields nanoparticles whose optical properties are reproducible. Additional characterization of the

nanoparticles was done by dynamic light scattering, transmission electron microscopy, and Raman spectroscopy.

COLL 283

Self-healing, antibacterial host-guest coating doped nanoparticles

Liqin Ge, lqge@seu.edu.cn. Southeast University, Nanjing, China

In the fields of food engineering such as delivery, storage and fresh of fruits and vegetables, the coatings can grow some bacteria to cause deterioration of fruits and vegetables under the humid conditions. So, antibacterial materials have been becoming a unique and popular topic. Because these materials are easy to be damaged that will influence their usage, self-healing materials have an attracted considerable interest in biomedical engineering, chemical engineering and food engineering. In our work, the MoS₂/β-CD-PEI/AD-PAA coatings based on the host-guest interactions were successfully fabricated on the substrate via the layer-by-layer self-assembly technique to achieve antibacterial and self-healing coatings. It could be found that the coatings exhibited so admirable self-healing capacity. And they are able to greatly suppress bacterial adhesion. Specially, under UV light irradiation, the MoS₂/β-CD-PEI/AD-PAA coatings can improve their antibacterial property obviously. This simple and easy approach to preparing the self-healing and antibacterial coatings offers unique development opportunities in the field of highly engineered materials, such as food packaging, for which safety, performance, and longer fatigue life are crucial smart factors.

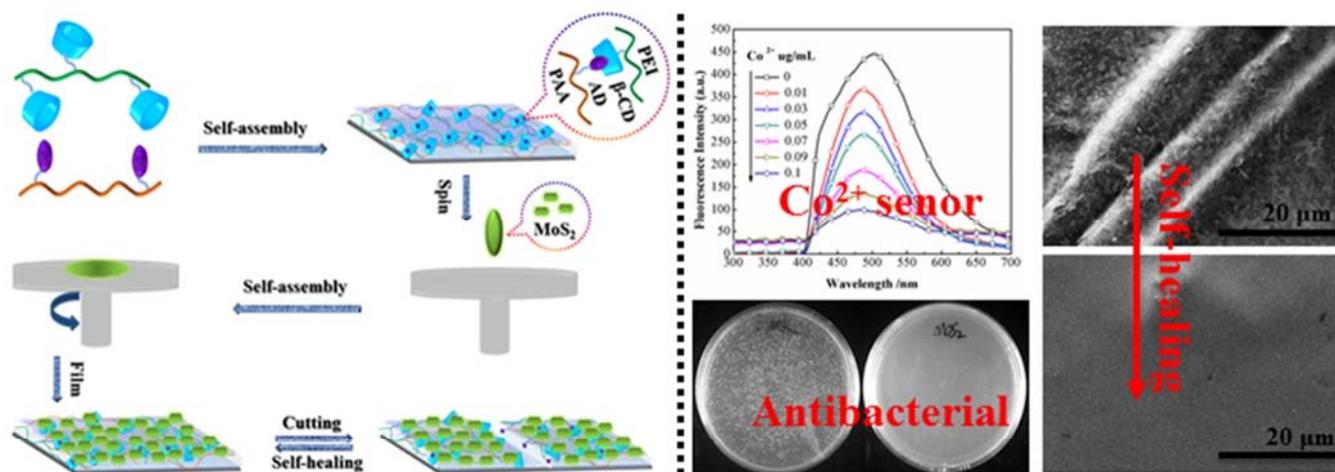


Figure 1. Novel MoS₂/β-CD-PEI/AD-PAA coatings with Co²⁺ sensing, antibacterial and self-healing properties are developed via the layer-by-layer (LbL) self-assembly technique.

Self-propelled water based organo-silanes on glass

Mitra Vasei, **Simon-Claude Poirier**, scpoirier@avmor.com. Research and Development, Avmor Ltd, Laval, Quebec, Canada

The self-motion of liquid droplets on solid surfaces has attracted broadening attention in last few years. Self-propulsion of a liquid occurs when a surface tension gradient causes the liquid to flow. The difference in surface tension on either side of a liquid droplet produces a directional transport of the droplet through a second liquid or over a solid substrate. This phenomenon is known as the Marangoni effect. A classic example of Marangoni effect is wine tears on the wall of a glass. Due to different evaporation rates of alcohol and water, a gradient of surface tension is created on the glass wall which causes wine moves upward. In artificial systems, a similar effect can be achieved for a droplet sitting on a homogeneous surface if the droplet contains a species which adsorbs/reacts onto the surface. Droplet motion is then driven by the irreversible modification of the surface free energy which affects the interfacial energy on either side of the droplet—a so-called “chemical” Marangoni effect.

In this study, we present water born fluoro-silane mixtures showing a self-propulsion behavior on glass. The movement can surmount the gravity force and push the droplet uphill (Figure.1). The droplet moves on the glass surface and changes the glass surface energy instantly by chemically bonding a silane based nano-layer onto the surface. The droplet velocity changes with the concentration of the fluoro-silanes composition, the pH, the critic micelle concentrations (CMC) as well as the surface tension of the solution organo-silane solution. A water-based droplet motion system could be an exceptional model of the process of chemo–mechanical energy conversion with variety of applications in microfluidics and delivery systems. Therefore, the Marangoni effect will be discussed in term of binding mechanism to the glass substrate.

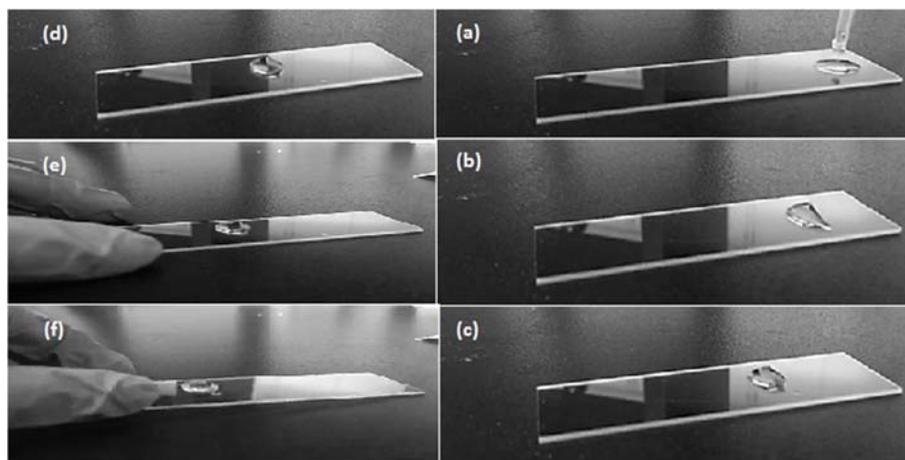


Figure-1. Self-propulsion effect on the surface glass.

COLL 285

Silica modified candle soot layer-based SERS substrates for the ultrasensitive detection of biological molecules

Weiping Qian, wqian@seu.edu.cn. Southeast University, Nanjing, China

Silica modified candle soot layer (SMCSL) exhibits excellent superhydrophobic property due to its uneven surface and low surface energy. Herein, we choose SMCSL as superhydrophobic platform for the fabrication of sensitive and reproducible SERS substrate by simply drying a droplet of colloidal suspension onto the SMCSL surface. We employed silver coating Au nanostars (AuNS@Ag) for the fabrication of SERS substrate due to their excellent optical properties. Densely-assembled AuNS@Ag on the SMCSL platform provide high density hot spots over the entire region of the substrate and improve the SERS activity. Additionally, analyte enrichment based on the superhydrophobic surface can also contribute to the ultrasensitive SERS detection. The as-prepared substrate, termed silver coating Au nanostars on the silica modified candle soot layer (AuNS@Ag/SMCSL), has exhibited high sensitivity and reproducibility of SERS signals. Our results suggest that assembling AuNS@Ag onto the SMCSL platform could provide a new route to fabricate low-cost, high-performance SERS substrates for the ultrasensitive detection of biological molecules.

COLL 286

Single-particle tracking for the routine characterization of polydisperse nanoparticle solutions

Xun Gong¹, xungong@mit.edu, Minkyung Park¹, Kevin Silmore¹, Dorsa Parviz¹, Tedrick Lew¹, Michael Strano². (1) Chemical Engineering, Massachusetts Institute of Technology, Somerville, Massachusetts, United States (2) Chemical Engineering, 66-566, MIT, Cambridge, Massachusetts, United States

Colloidal dispersions of nanomaterials are often polydisperse, particularly early on in their early development, due to factors relating to synthetic control, dispersion efficiency and instability during storage. As their targeted applications often depend on their dimensional parameters, monitoring changes in the size and aspect ratio distribution between multiple samples or the same sample over time is paramount. The most commonly employed methods in the literature, such as dynamic light scattering, only estimate the first or second moment of narrow distributions. In this work, we introduce a rapid analysis employing single particle tracking (SPT) demonstrate its ability to probe solution particle distributions of common preparations of single-walled carbon nanotubes (SWCNTs) and graphene oxide (GOx) at different stages of centrifugation. Our results demonstrate that SPT is able to measure distribution changes throughout the course of material preparation, and consequently, dispersion quality and the effectiveness of current protocols. Methodological comparison with analytical centrifugation (AUC) reveals that SPT is a facile analytical method with minimal biases

and expertise required, making it more attractive for routine characterization. As both SPT and AUC independently provide aspect ratio information for disk and rod like particles, their combination can allow for the determination of particle dimensions in the case of a highly monodisperse preparation. For example, a sample of SDS conjugated SWCNT was found to have a hydrodynamic radius and length of 2.8 nm and 308 nm respectively.

COLL 287

Solution synthesis of rectangular copper nanotubes and gold nanohelices

Yu-Hsu Chang, *yhchang@ntut.edu.tw*, Yao-Chun Chang. *Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan*

Rectangular copper nanotubes (rCu NTs) and gold nanohelices (Au NHs) are synthesized on a large-scale using surfactant-assisted galvanic replacement reactions on rough aluminum substrates. In an acidic environment, Cu(II) is reduced on sharp-topped Al substrates and rCu NTs 150–300 nm in diameter and 2–10 μm in length are formed through fine-tuning the reaction temperature and chemical stoichiometry. Field-emission measurement results show that the rCu NTs emitting electrons at turn-on fields of $8.76 \text{ V } \mu\text{m}^{-1}$ is observed with a field enhancement factor of 85. The superior catalytic property of rCu NTs in the degradation of a methylene blue aqueous solution in the presence of H_2O_2 is also presented.

For the synthesis of Au NHs, two chemical routes including galvanic replacement reaction and seed-mediated growth are employed and both of these two methods are able to form helical products with different morphology. Three surfactants, namely cetyltrimethylammonium bromide, polyvinylpyrrolidone, and poly(ethylene glycol)(12)tridecyl ether, act as capping agents to control appearance and size. Transmission electron microscopy analysis shows that the Au NHs are face-centered cubic in structure and that growths on the {111} facet are growth twins with mirror symmetry. Used as the substrate for surface-enhanced Raman scattering, the helical structure of the Au NHs creates numerous hot spots, exhibiting a superior surface enhancement effect

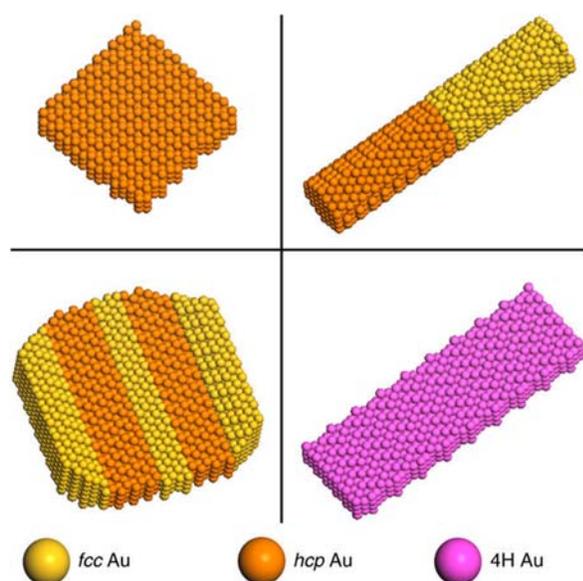
COLL 288

Solution-based crystal phase engineering of noble metal nanostructures

Ye Chen, *chen1023@e.ntu.edu.sg*, Zhanxi Fan, Hua Zhang. *Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore*

Wet-chemical synthesis is a classic method for metal nanostructures with scalability and relatively low cost. Various shapes, sizes, and crystal phases of metal nanocrystals can be obtained by simply tuning the reaction parameters. In this poster, our recent work on the crystal phase engineering of noble metal structures via wet-chemical routes is

introduced. First, colloidal solution based syntheses of Au nanostructures with unconventional crystal phases, including hexagonal close-packed (*hcp*), 4H, and 4H/face-centered cubic (*fcc*) crystal phase heterostructures, are summarized. Second, we report the surface modification-induced phase transformation of Au nanosquare sheets from *hcp* to *fcc* and of Au nanoribbons from 4H to *fcc*. Third, the templated epitaxial growth of single- and multi-metallic 4H and 4H/*fcc* noble metals on 4H Au nanoribbons and 4H/*fcc* nanorods to form various core-shell heterostructures are introduced. Both epitaxial growth and random continuous growth have been realized. Last but not the least, as a proof of concept, the superior catalytic performance of Au@PdAg nanoribbons on hydrogen evolution reaction and 4H/*fcc* Au@Pd nanorods on ethanol oxidation reaction are demonstrated.



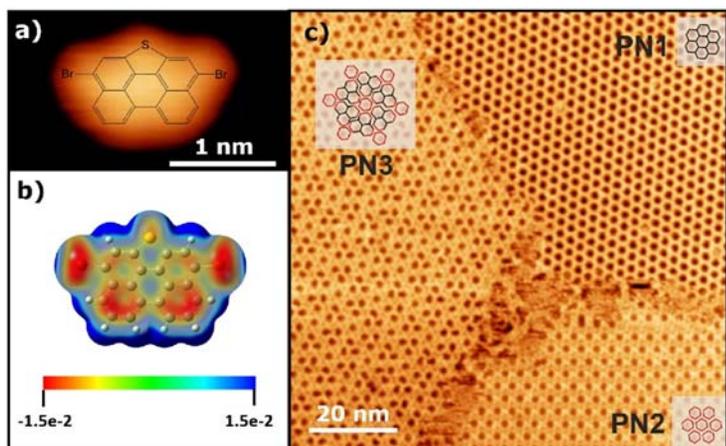
COLL 289

Steering DBPET porous networks by the co-play σ -hole interactions of Br[⋯]S & Br[⋯]Br

Lingbo Xing¹, xl0223@pku.edu.cn, **Zhichao Huang**¹, **Kai Wu**². (1) College of Chemistry and Molecular Engineering, Peking University, Beijing, China (2) College of Chemistry Molecular Eng, Peking University, Beijing, China

σ -hole bond is a noncovalent interaction due to the anisotropy of the charge distribution between a covalently-bonded atom of Groups IV–VII and a negative site, e.g. a lone pair of a Lewis base or an anion. Halogen bonding is a typical subset of σ -hole interactions. Herein, we investigate self-assembled behaviors of 3,10-dibromoperlylo[1,12-bcd] thiophene (DBPET) on Ag(111) by means of scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Three types of porous networks can be fabricated steered by the co-play σ -hole interactions of Br[⋯]S

and Br⁻Br⁻. For the first time, Sulfur-halogen electrostatic interactions act as the driven force of molecular assembly on metal surfaces.



COLL 290

Study of the influence of pH and ionic strength on the stability of melamine formaldehyde (MF) resin by field flow fractionation technique

Lambros Farmakis¹, lafarmakis@gmail.com, **John Kapolos**², jkapolos@teikal.gr, **Athanasia Koliadima**¹, akoliadima@chemistry.upatras.gr. (1) Chemistry, University of Patras, Patras, Greece (2) Food Technology, Technological Institute Of Peloponnese, Kalamata, Greece

Melamine and melamine-formaldehyde (MF) resin are both commonly used materials. At high temperature, melamine is formed by the decomposition of methylmelamine, an intermediate of MF composition. The stability of aqueous solutions of MF resins during storage is limited in environmental temperature, but it is shown in this work that it is strongly influenced by the ionic strength and the pH value of the suspending medium. Aggregation phenomena, polymerization or disintegration of MF resin particles can take place. The critical aggregation concentration (CAC) and the rate constant k_{app} for the bimolecular process of aggregation are also determined. For this study, Field Flow Fractionation (FFF) technique was used, which is a very promising elution technique for the separation and characterization of colloidal materials and macromolecules.

COLL 291

Successive ultraviolet irradiation of mixed monolayers removes molecules and re-orders self-assembled domains

Cynthia Gerber, cynthia.gerber@uconn.edu, **Rebecca Quardokus**. Chemistry, University of Connecticut, Willington, Connecticut, United States

Self-assembled monolayers (SAMs) consist of a single layer of molecules that form long-range order due to intermolecular interactions such as hydrogen bonding and van der Waals forces. Manipulation of mixed SAMs have the potential to control the functionality of a surface by facilitating multi-molecule organization. We study the effects of ultraviolet radiation on a mixed-monolayer of anthracene dicarboxylic acid and octanethiol using scanning tunneling microscopy. The ultraviolet light disrupts the SAM by removing individual octanethiol molecules and reorganizing the monolayer. Initial exposure creates highly disordered regions on the surface, but prolonged exposure restores order by reorganizing the octanethiol into ordered domains. The ability to manipulate and control SAMs shows exciting potential for their use in next-generation molecularly based devices.

COLL 292

Supramolecular assembly onto polymer-supported Au monolayers fabricated *via* chemical lift-off lithography

Gail A. Vinnacombe^{1,4}, vinnacombe@chem.ucla.edu, Kevin M. Cheung^{1,4}, Grace E. Kunkel², Ashley E. Trojniak², Alyssa VanZanten², Mary E. Anderson^{2,3}, Paul S. Weiss^{1,4}. (1) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California, United States (2) Chemistry, Hope College, Holland, Michigan, United States (3) Chemistry, Furman University, Greenville, South Carolina, United States (4) California NanoSystems Institute, UCLA, Los Angeles, California, United States

We employ chemical lift-off lithography (CLL) - a scalable and economical subtractive patterning technique - to create patterned Au monolayers supported on flexible polymers. In this work, we explore the supramolecular assembly of metal-organic multilayers (MLs) and surface-tethered metal organic frameworks (SurMOFs) on this hybrid material. We characterize the growth using atomic force microscopy, X-ray photoelectron spectroscopy, UV-visible spectroscopy, and contact angle goniometry. Thin films of α,ω -mercaptoalkanoic acids and Cu^{2+} have been used to form hierarchical structures on metal substrates using robust chemical interactions. Studies on MLs yield important fundamental knowledge regarding molecular self-assembly, while also finding applications in nanoscale electronics and anti-fouling coatings. Similarly, metal-organic frameworks (MOFs) rely on metal-organic interactions to form unique porous structures, which enable selective gas up-take. The integration of MOFs into functional electronic devices, photovoltaics, and optical sensors has been realized with the development of SurMOFs. We target supramolecular assembly of the HKUST-1 MOF *via* liquid-phase epitaxy onto underlying hydroxyl ($-\text{OH}$) and carboxy ($-\text{COOH}$) terminations. Through CLL, we take advantage of facile nanoscale pattern fabrication to move towards strategic patterning of metal-organic assemblies on flexible, transparent substrates by controlling surface functionality.

COLL 293

Surface chemistry and spectroscopy study of α -synuclein and the NAC part

Oladimeji Olaluwoye, Saad Alrashdi, Ricardo Castillo, Chengshan Wang, wcslove@hotmail.com. Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee, United States

Parkinson's disease is the second most common neurodegenerative disease and is characterized by a progressive loss of the dopaminergic neurons in *substantia nigra*. The degenerating dopaminergic neurons develop a hallmark deposition of Lewy bodies comprising abundant abnormal aggregates (i.e., fibrils) of α -synuclein (α -syn), which is a protein contains 140 amino acid residues. Despite the abundance ($\sim 1\%$ among the total proteins) in the brain, α -syn accumulates in the presynaptic terminals where exists high concentration of amphiphilic structure (e.g., liposomes and cell membrane) and the reason of the accumulation is not clear. On the other hand, the primary structure of α -syn constitutes three domains: N-terminal residues 1–60; the nonamyloid component (NAC) which spans residues 61–95 and is responsible for the aggregation; and residues 96–140 which comprise the negatively charged C-terminus. Here, both α -syn and its NAC part (i.e., α -syn(61-95)) were synthesized and purified. α -Syn and α -syn(61-95) were shown to be able to form a stable Langmuir monolayer at the air-water interface by Langmuir technique, which utilizes air-water interface to mimic the amphiphilic structure in vivo. From circular dichroism and FTIR results, both α -syn and α -syn(61-95) transform from unstructured conformation in aqueous solution to α -helix at the interface. Because α -helix is stable at the interface, this transformation explains the reason of the accumulation of α -syn around the amphiphilic structure. α -Syn(61-95), the NAC part of α -syn, did not aggregate at the interface. This also suggests the amphiphilic structure stabilizes α -syn and inhibits its aggregation. The onset of Parkinson's disease may be due to the lost of amphiphilic structure (such as phospholipids) in the brains of aging people.

COLL 294

Surface engineering of graphene materials for advancing antimicrobial performance

Wantae Kim^{1,2}, 123456@kaist.ac.kr, JeGoo Son^{1,3}, Hyun Cho^{1,2}, Seunggyu Kim^{1,3}, Jessie S. Jeon^{4,3}, Eun Seon Cho^{1,2}. (1) Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of) (2) Department of Chemical & Biomolecular Engineering, KAIST, Daejeon, Korea (the Republic of) (3) Mechanical Engineering, KAIST, Daejeon, Korea (the Republic of) (4) KAIST, Daejeon, Korea (the Republic of)

Graphene-based materials are an attractive template for a broad range of applications due to their unique 2D structure and excellent physiochemical properties, allowing us to address global challenges. A general approach to prepare graphene-based materials is

to utilize graphene oxide (GO) which possesses various oxygen functional groups on its basal plane and edge site. Combined with a large surface area and tunable functionality through surface chemistry, GO is a promising material for the design of engineering surfaces. In biomedical and environmental applications, several groups have reported that graphene materials present an antimicrobial effect against a variety of microorganisms, in which it includes controlling the growth of bacteria. Antimicrobial mechanism of graphene materials has not been exactly clarified; however, prevalently the induction of physical damage of the lipid bilayer and the generation of chemically reactive species are considered as a major mechanism. For the chemical mechanism, the reactive species can be produced through the functional groups on graphene materials, which mediates oxidative stress. Among different kinds of graphene materials, only GO has been extensively investigated as an antimicrobial substance; hence, the chemically induced antimicrobial effect was exclusively focused on reactive oxygen species (ROS). In this study, we investigated the antimicrobial effect of graphene materials doped with different reactive elements such as oxygen, sulfur, chlorine, and nitrogen. It allows us to examine the influence of different reactive species on antimicrobial activity of graphene materials, correlating it with oxidative stress. The antimicrobial properties of graphene-coated surface were probed via a direct contact with both Gram-negative and -positive bacterial pathogens, in which the surface-dependent of antimicrobial activity was quantified through the live/dead fluorescence of such bacteria. This analysis can contribute to the development of antimicrobial surface for biomedical and display devices without releasing toxic substances into environment. Further, our study will help to understand the antimicrobial mechanism of graphene materials by evaluating their ROS-independent oxidative stresses with various reactive species.

COLL 295

Surface functionalization of cationic SDBS/CTAT vesicles

Matthew Hurley¹, mhurley@anselm.edu, Paul Zayka¹, Elizabeth Holt¹, Nicholas Soto², Elizabeth Robinson², Philip R. DeShong². (1) Chemistry, Saint Anselm College, Manchester, New Hampshire, United States (2) Chemistry and Biochemistry, University of Maryland, College Park, College Park, Maryland, United States

Anionic SDBS/CTAT vesicles spontaneously form when SDBS and CTAT are mixed in a 3:1 molar ratio at specific concentrations. The vesicles are stable, spherical surfactant bilayers with an average diameter of 150 nm and a zeta potential of -50 mV.

SDBS/CTAT vesicles have potential to serve as targeted-drug delivery systems. Small, hydrophobic molecules can be incorporated into the vesicles—demonstrating their ability to carry a drug payload. To create vesicle-based targeted drug delivery systems, the vesicles must be functionalized with targeting molecules that direct the vesicles to specify tissues within the body. Functionalized vesicles can be prepared by anchoring molecules to the surface of vesicles. In this study, different methods to anchor carbohydrate and protein conjugates to vesicles were evaluated. Molecules can associate with vesicles through hydrophobic interactions with the surfactant bilayer and

through electrostatic interactions with the anionic vesicle surface. Carbohydrate and protein derivatives containing different anchoring moieties were tested to identify anchoring moieties that associate with vesicles most readily. Results indicate that slight variations between anchor moieties can significantly affect the ability of the conjugates to associate with vesicles.

COLL 296

Sustainable glucose oxidation with enzymatic magnetically recoverable catalysts

Bret Lawson¹, bpatlawson202@yahoo.com, **Ekaterina Golikova**², **Aleksandrina Sulman**², **Barry D. Stein**³, **Natalya Lakina**², **Alexey Karpenkov**⁴, **Esther Sulman**², **Valentina Matveeva**², **Lyudmila Bronstein**^{1,2}. (1) Chemistry, Indiana University Bloomington, Bloomington, Indiana, United States (2) Biotechnology and chemistry, Tver Technical University, Tver, Russian Federation (3) Biology, Indiana University Bloomington, Bloomington, Indiana, United States (4) Tver State University, Tver, Russian Federation

Monosaccharide oxidation, such as the oxidation of D-glucose to D-gluconic acid, received considerable attention for the production of drugs, supplements, cleaning product components and more. We report magnetically recoverable biocatalysts for enzymatic oxidation of D-glucose to D-gluconic acid with high product yields. The catalyst is based on nanoparticle clusters (NPCs) composed of magnetite particles, coated with an amino terminated silica layer for further attachment of a glutaraldehyde linker and glucose oxidase (GOx). It was observed that the NPCs with a diameter of ~430 nm attach 33% more GOx molecules than NPCs with a diameter of ~285 nm; this is most probably due to lower curvature of the former. At the same time, the biocatalyst containing the smaller NPC core shows higher relative activity of 94% than that of the biocatalyst based on the larger NPCs (87%), at optimal reaction conditions. We believe this phenomenon is due to (i) GOx crowding on the support surface, which should prevent denaturation (similar to the enzyme behavior in cells) and (ii) variations of enzyme mobility which should be preserved upon immobilization of the enzyme. Apparently, for the biocatalyst based on 285 nm NPCs, the lower GOx crowding is compensated by its higher mobility. High stability of this catalyst and easy magnetic recovery as well as excellent catalytic activity in a wide pH range make this biocatalyst promising for practical applications.

COLL 297

Synergistic nanosponge-antibiotic therapy for the treatment of biofilm associated infections

Cheng Hsuan Li, chenghsuanli@umass.edu, **Xinghong Chen**, **Ryan Landis**, **Akash Gupta**, **Jessa M. Makabenta**, **Vincent M. Rotello**. Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Antibiotics are the standard therapeutic treatment for bacterial infections. However, bacterial infections often develop into biofilms, which are resistant to penetration by antibiotics. In addition, the efficacies of antibiotics are often limited due to their poor water solubility. Here, we present a polymer-stabilized phytochemical core nanosponge that shows excellent ability to penetrate biofilms. Furthermore, antibiotics can be loaded into these nanosponges to improve their efficacy through their enhanced penetration into the biofilm matrix and through synergy/additive effects between the antibiotic and the phytochemical. Taken together, this strategy provides promising anti-biofilm therapies.

COLL 298

Synthesis and characterization of composition-controllable platinum-copper-cobalt nanoalloy catalysts

Dominic Caracciolo, dcaracc2@binghamton.edu, Daniel M. Adrion, Shiyao Shan, Richard Robinson, Jin Luo, Chuanjian Zhong. Dept of Chemistry, State University of New York at Binghamton, Binghamton, New York, United States

Fuel cells represent a promising vector of clean energy to improve the quality of life and for a cleaner environment. However, major challenges in the existing fuel cell devices include the sluggish cathode reaction and the high amount of platinum group metals in the catalysts. It is of great importance to develop catalysts with lower cost and higher activity and stability. In this work, we focus on the synthesis of multimetallic nanoparticle catalysts by alloying platinum with other low-cost transition metals such as copper and cobalt. By alloying, not only the cost is reduced but the stability and the activity are also significantly enhanced. The results from an investigation of the synthesis and preparation of platinum-copper-cobalt nanoalloys with tunable size and composition will be discussed. The detailed morphological and structural characterizations of the ternary nanoalloys will also be discussed, attempting to better understand the nanostructural correlation with the catalytic properties.

COLL 299

Synthesis and evaluation of polyglycerol carbonate/polyester blend nanocarriers for paclitaxel delivery

Rob Sabatelle¹, rsabs@bu.edu, Iriny Ekladiou¹, Nitinun Varongchayakul¹, Catalina Bordeianu¹, Yolonda L. Colson², Mark W. Grinstaff¹. (1) Boston University, Boston, Massachusetts, United States (2) Department of Surgery, Brigham and Women's Hospital, Boston, Massachusetts, United States

Polymeric nanoparticles (NPs) are widely employed as cancer nanomedicines due to their ability to more effectively deliver cytotoxic chemotherapeutics such as paclitaxel (PTX). PTX is commonly used to treat a variety of solid organ malignancies, but suffers from poor solubility, rapid clearance, and low target tissue concentrations. NPs can be

utilized to control drug release kinetics and increase drug delivery efficiency. Interestingly, particle stiffness modulates cellular internalization and nanocarrier efficacy, warranting further study and optimization of nanomechanical properties. In particular, softer structures generally exhibit more rapid cellular internalization and enhanced potency. However, despite the potential impact of nanoscale mechanics, relatively few studies modulate nanoparticle core composition in order to decrease stiffness and optimize therapeutic efficacy. We have previously demonstrated sustained and efficient PTX delivery using poly(1,2-glycerol carbonate)-*graft*-succinic acid-paclitaxel (PGC-PTX) conjugate NPs. Encapsulation of free PTX within the PGC-PTX NP core increases core interactions and, consequently, particle stiffness. In contrast, the incorporation of a more hydrophilic polymer, such as poly(lactide-co-glycolide) (PLGA) or polypropylene glycol (PPG), can potentially disrupt compact aggregation in the hydrophobic polymer core and reduce particle stiffness. We herein evaluate the modulation of nanocarrier mechanical properties as well as efficacy through the incorporation of additional polymers such as PLGA and PPG. Specifically, we report the preparation, characterization, and evaluation of the *in vitro* cytotoxic activity of PGC-PTX/PLGA and PGC-PTX/PPG polymer blend nanocarriers.

COLL 300

Synthesis and properties of surface functional hyperbranched polymer nanoparticles

Yeshin Lee, yesin93@catholic.ac.kr, Byeong-Kwan An. Department of Chemistry, The Catholic University of Korea, Bucheon-si, Gyeonggi-do, Korea (the Republic of)

Polymer nanoparticles (PNPs) with monodispersed sizes and shapes have been received much attention in various industrial applications such as catalysts, coating materials, chemical sensors, drug deliveries, adsorbents and optoelectronic devices, owing to their distinctive properties. The key properties of these well-defined PNPs can be controlled and modified by the surface functional groups. As a result, many types of PNPs having specific functional groups on the surface have been developed so far in order to achieve the desired properties for a particular application. In this work we report a simple and efficient method of fabricating hyperbranched polymer nanoparticles (HB-PNPs) bearing phenolic units on the surface. The target HB-PNPs with size in the range of 300-400 nm were prepared in high reproducibility by the emulsifier-free polymerization. The obtained HB-PNPs showed high chemical, thermal and mechanical stability due to the cross-linking structure of polymers. Additionally, it was found that the phenolic surface groups of HB-PNPs are versatile to be served as an acid catalyst and functionalized with fluorescent dyes.

COLL 301

Synthesis and self-assembly of magnetoplasmonic nanoparticles

Derong Lu, *derong.lu@uq.net.au*. SCBE, Nanyang Technological University, Singapore, Singapore, Singapore

The development of magnetoplasmonic nanomaterials is a topic of considerable interest because of the combination of plasmonic and magnetic properties. The plasmonic component allows optical detection, photothermal therapy (PTT), and photoacoustic imaging (PAI), while the magnetic part provides magnetic targeting, Magnetic resonance imaging (MRI), and magnetic hyperthermia. Multifunctional magnetoplasmonic nanoparticles, which can be utilized for synergistic optical/MRI imaging and photothermal/hyperthermia therapy, lead to the new approaches for overcoming the restrictions of current diagnostic tools.

Magnetoplasmonic Janus nanoparticles (e.g., Au@Fe₃O₄) offer unique features, including the precisely controlled distribution of compositions, surface charges, dipole moments, modular and combined functionalities, which enable excellent applications that are unavailable to their symmetrical counterparts. Assemblies of NPs exhibit coupled optical, electronic and magnetic properties that are different from single NPs. Through bringing together advances in nanochemistry, polymer chemistry, self-assembly, and nanophotonics, we expect to further expand our capability of tailoring optical and structural characteristics of Magnetoplasmonic assemblies not only provide a new insight into the self-assembly mechanism of polymer/inorganic nanoparticles but also address challenges in nanomedicine area.

COLL 302

Synthesis of alkanethiolate-capped palladium nanoparticles through reversed alkyl thiosulfate addition to control core size & tune surface ligand density

Kevin M. Vargas, *kevinvargascollege@gmail.com*, *Khin Aye San*, *Young-Seok Shon*. *Chemistry and Biochemistry, California State University, Long Beach, Long Beach, California, United States*

Ligand-capped metal nanoparticles exhibit promising properties as catalysts. Its large surface to volume ratio allows for high catalytic activity, while its ligands dictate the immediate environment around the catalytic surface, allowing for directed catalytic selectivity. Alkanethiolate-capped palladium nanoparticles (PdNPs) have previously been synthesized using a modified Brust-Schiffrin synthesis (using alkyl thiosulfate instead of alkanethiol), in which the nanoparticle core size is established during alkyl thiosulfate ligand passivation of the nanoparticle nucleation-growth initiated by borohydride reduction. Due to the dependence of core size on amount of ligand present, surface ligand density decreases with increasing core size. Herein we present a method in which core size is established independent to ligand addition, allowing the formation of PdNPs with similar core sizes, yet different surface ligand density. In this method, core size is established during the temporary passivation of growing nanoparticles by borohydride and tetraoctylammonium bromide (TOAB), allowing nucleation to reach completion. Various molar equivalents of alkyl thiosulfate are then added, prompting the replacement of borohydride and TOAB and the formation of alkanethiolate-capped

PdNP. The resulting PdNPs were characterized via ¹H NMR, UV-Vis spectroscopy, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), FT-IR, and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Overall enhanced catalytic activity of hydrogenation/isomerization of dienes and alkenes was observed for PdNPs with a lower ligand density, proving the isolated effect of surface ligand density from other variations such as core size and shape.

COLL 303

Synthesis of composition tunable platinum-based ternary nanoalloy catalysts for fuel cell applications

Zhi-Peng Wu¹, zpwu1109@gmail.com, Emma Hopkins¹, Keonwoo Park¹, Shan Yan¹, Jie Wang², Jianguo Wen², Jin Luo¹, Lichang Wang³, Chuanjian Zhong¹. (1) Dept of Chemistry, State University of New York at Binghamton, Binghamton, New York, United States (2) Electron & X-ray Microscopy, Nanoscience and Technology, Argonne National Laboratory, Lemont, Illinois, United States (3) Chemistry Biochemistry M/C 4409, Southern Illinois University, Carbondale, Illinois, United States

Fuel cells with high energy conversion efficiency, renewable sources, and low environmental pollution are expected to come into widespread commercial use, but a key challenge is the lack of low-cost, active and robust catalysts for fuel cell reactions. In this work, we focus on developing the ability to finely control the composition and nanostructure of ternary Pt-based catalysts for fuel cell reactions. Composition-tunable Pt-based ternary catalysts are synthesized by varying the feeding ratios and the reaction temperatures using the wet chemical method. The catalysts are examined by electrochemical experiments to access the catalytic activity for oxygen reduction reaction (ORR). Density functional theory computation is also performed to further assess the relationship among the composition, structure, and activity of the catalysts. Implications of the results for the design, synthesis, and preparation of low-cost and highly-active catalysts for fuel cells will also be discussed.

COLL 304

Synthesis of eco-friendly biosurfactants from vegetable oils and characterization of interfacial properties for cosmetics and household products

DaNan Yea, SeonHui Jo, **JongChoo Lim**, jongchoo@dongguk.edu. Chemical and Biochemical, Dongguk University-Seoul, Seoul, Korea (the Republic of)

Recently, interest in biosurfactants has been steadily increasing due to their diversity, environment friendly nature such as nontoxicity and excellent biodegradability, possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection. Due to their unique functional properties, biosurfactants have been used in various industries including agriculture, fertilizers, petroleum, petrochemicals, cosmetics, pharmaceuticals, personal care

products, food processing, beverages, textile manufacturing, metal treatment and processing, pulp and paper processing, paint industries and many others. In this study, amino acid based biosurfactants were synthesized from renewable vegetable oils. The structure of the resulting products was elucidated by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopies and environmental compatibility such as biodegradability and acute oral toxicity was evaluated. The interfacial properties of synthesized surfactants have been also examined such as critical micelle concentration (CMC), static and dynamic surface tensions, interfacial tension, wetting property, emulsion stability, viscosity, and foam property. The results indicated that synthesized surfactants have excellent interfacial properties. Detergency test has been performed with newly synthesized surfactants by using an agitation/mixing type detergency tester at room temperature. The results suggested that the newly synthesized surfactants show moderately good detergency. Acute oral toxicity (LD_{50}) measurement showed that newly synthesized surfactants are very mild compared with conventional nonionic and anionic surfactants used in detergent and cosmetic formulations such as polyoxyethylene (9) lauryl ether (PLA) and dodecylbenzene sulfonic acid (LAS). The primary biodegradability of newly synthesized surfactants has been found to be greater than 95%, suggesting that newly synthesized surfactants are acceptable for cosmetic and detergent applications. Both acute dermal irritation and acute eye irritation tests revealed that surfactants are mild. In particular, the prescription test in shampoo formulation prepared with synthesized biosurfactants indicated better sensory feeling and excellent foaming ability compared with conventional surfactants used such as silicon. The patch test also indicated no irritation during 48 hours, indicating potential applicability in cosmetic and household products.

COLL 305

Synthesis of high quality bio-graphene suspensions in water for use in a nyctinastic radiator for outer space solar arrays

Megan K. Puglia¹, *megan.puglia@uconn.edu*, **Mark O'Neill**², **Challa V. Kumar**³. (1) *Chemistry, University of Connecticut, Storrs, Connecticut, United States* (2) *Mark O'Neill, LLC, Keller, Texas, United States* (3) *Univ of Connecticut, Storrs Mansfield, Connecticut, United States*

Thermal management of solar arrays destined for outer planetary missions is a critical unmet challenge. Graphene-based radiators that would autonomously dissipate heat from a solar array are an attractive solution due to the high thermal conductivity of single layer graphene. However, single layer graphene is very expensive and alternatives to this material are highly desired. In this context, we report a simple, environmentally friendly, non-labor intensive method for the synthesis of colloidal graphene suspensions of 3-5 layers, stabilized by bovine serum albumin, in water. The method involves a flow reactor designed to continually yield high quality graphene colloids, synthesized, purified and optimized all in one set-up. The flow reactor is able to produce colloidal graphene sheets on a multi-gram scale and these colloids were characterized by Raman spectroscopy, electron microscopy and zeta potential studies. The average size of the sheets is 0.5 μm , each consisting of 3-5 layers of graphene with

little or no sp₃ defects. These graphene colloids stabilized by the protein were coated onto a number of different substrates and their lateral thermal conductivities were measured using a homemade apparatus. The thermal conductivities are comparable to those reported in the literature but showed a significant trend. The ease of synthesis of these high quality graphene colloidal suspensions in water provides an exciting opportunity for bio-graphene to be used on an industrial scale for electronic, thermal and enzymology applications.

COLL 306

Synthesis of mesoporous silica decorated with titania nanoparticles and their photocatalytic activities

Bomin Kim¹, *clairkim06@gmail.com*, **Arum Jung**³, **Myonghoo Hwang**², **Bongjun Yeom**². (1) *Chemical engineering, Hanyang university, Seoul, Korea (the Republic of)* (2) *Hanyang university, Seoul, Korea (the Republic of)* (3) *Hanyang University, Seoul, Korea (the Republic of)*

Mesoporous silica with large surface area has attracted much attentions as a potential candidate material for the support of catalytic nanomaterials. Titania (TiO₂) nanoparticles have photodegradability for organic materials and their catalytic reactions are dependent to their morphology and crystallinity. In this study, we investigated synthesis methods for the preparation of titania/mesoporous silica(SBA-15) composite materials and their photocatalytic properties. The different amounts of titania nanoparticles were post-impregnated into mesoporous silica using sol-gel method and layer-by-layer assembly method. We examined dispersion and characteristics of mesopores and crystallinity of titania nanoparticles, and further evaluated the photocatalytic performances on the decomposition of methyl orange in aqueous solutions. We could observe that such catalytic reactions are crucially dependent to the crystallinity and dispersion of titania nanoparticles. We believe this work could help in design of photocatalytic nanomaterials for antimicrobial coatings and environmental applications.

COLL 307

Synthesis, characterization and potential applications of nanoparticles based on naturally-occurring polymers

Olga Kvak, *olga.kvak@mail.utoronto.ca*, **M. Cynthia Goh**. *Department of Chemistry, University of Toronto, Toronto, Ontario, Canada*

The collapse of polyelectrolytes by counterion condensation has been a topic of interest for the last half-century. Goh's lab has previously demonstrated the ability to manipulate polyelectrolyte conformation in the presence of counterions as a general way to make polymer-encapsulated nanoparticles. The charged polymer can exist in the extended chain conformation due to the repulsion of same charges along the chain. Introduction

of counter-ions collapses the polymer by masking or neutralizing these charges, leading to a more compact nano-structure, where the resulting size is restricted by the collapse of the polymer of choice. This technique has been employed in making various types of materials – e.g., metals, oxides, quantum dots – within a polyacrylic acid nanoparticle. In this work, a similar approach is utilized as applied to naturally occurring polymers, such as hyaluronic acid (HA) and alginic acid (AL), which are of great interest as topical delivery systems. The nanoparticles formed are stabilized by covalent cross-linking HA or AL polymer using 1,6-hexanediamine in the presence of a water-soluble carbodiimide. Particle sizes were examined using kinematic viscosity (St), dynamic light scattering (DLS), and atomic force microscopy (AFM).

COLL 308

Synthesis, self-assembly and gelation studies of ninhydrin based unnatural α -amino acids as low molecular mass gelators

Farzana Zerín, fzerin@ggc.edu, Joseph Sloop, Ajay V. Mallia. School of Science and Technology, Georgia Gwinnett College, Lawrenceville, Georgia, United States

Low molecular mass gelators are viscoelastic materials that can be considered as an important class of soft materials. The gelator molecule aggregate *via* weak intermolecular interactions such as hydrogen bonding, van der Waals interactions and π - π stacking to form a three dimensional fibrillar network that can trap large amount of liquid. Among the low molecular weight gels, amino acid based gelators are important due to their biocompatibility and potential therapeutic applications. In the present work unnatural α -amino acids (1, 3-dioxo-2-(phenylamino)-2, 3-dihydro-1H-indene-2-carboxylic acid derivatives) have been prepared using the Bargellini condensation reaction between ninhydrin and 4-substituted anilines (substituent = H, OCH₃, OCF₃ and OC₈H₁₇) [3]. 5 wt % of 1,3-dioxo-2-(4-octyloxyphenylamino)-2,3-dihydro-1H-indene-2-carboxylic acid has been shown to gelate isopropanol and silicone oil, whereas the trifluoromethoxy derivative (1,3-dioxo-2-(4-trifluoromethoxyphenylamino)-2,3-dihydro-1H-indene-2-carboxylic acid) gels silicone oil and safflower oil. Correlations between the molecular structures of the amino acid gelators and the properties of their gels, including critical gelator concentrations, periods of stability, and gel-sol transition temperatures, thermodynamic and spectroscopic properties will be presented.

COLL 309

Targeted gene regulation by an enzyme degradable nucleic acid nanocapsule

Alyssa Hartmann, alyssa.hartmann@uconn.edu, Dominic Cairns-Gibson, Halle Barber, Jessica L. Rouge. Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States

GATA-3 is a transcription factor that is responsible for the differentiation of Th2 cells in inflammatory pathways. Due to this critical role in differentiation, targeted silencing of the GATA-3 gene has shown promise as a potential target for the treatment of inflammatory diseases. Recently a GATA-3 specific DNAzyme – a catalytically active DNA molecule – has been shown to specifically bind and cleave GATA-3 mRNA. Oftentimes highly folded nucleic acids such as DNAzymes must be chemically modified or assisted in their entry into cells by chemical transfection agents in order to maintain their chemical stability. In light of this limitation, our group has recently developed a nucleic acid nanocapsule (NAN) for delivering unmodified nucleic acid ligands with a built-in mechanism for deployment when endocytosed. We have shown that functionalization of the NAN with the GATA-3 specific DNAzyme results in a construct that is readily taken up into cells without the need for external transfection agents and which maintains its cleavage activity. Herein we show that DNAzyme NAN (DNz-NAN) can cleave truncated GATA-3 mRNA in solution, and full length GATA-3 mRNA in MCF-7 cells as quantified by qPCR, showing that the DNAzyme is able to retain its catalytic activity post attachment to the nanocapsule. Taken together the DNz-NAN has the potential to both silence a gene through mRNA cleavage while simultaneously releasing an internalized small molecule cargo. This route to co-delivery can enable the synergistic release of a therapeutic oligonucleotide and small molecule drug, with important implications in the treatment of a variety of inflammatory diseases.

COLL 310

The assessment of bacterial interactions with surfaces through the estimation of the adsorption free energy

Nick Kotoulas, nicholas.kotoulas@mail.utoronto.ca, M. Cynthia Goh. Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

While it is clear that there would be differences in interactions between different bacteria and different surfaces, there is no simple way of measuring such. This work aims to find a way by which this interaction can be derived semi-quantitatively. Surfaces that would offer different types of interaction (positive, negative, hydrophilic, hydrophobic) were prepared by adsorbing polyelectrolytes to a glass slide, which then formed the wall of a microfluidic channel through which the bacterial solution was passed. The number of bacteria in the bulk was obtained by measurement of the optical density of the solution, while the amount adsorbed at a specific bulk concentration was determined by direct observation using optical microscopy. The results were analyzed in terms of adsorption isotherm models to extract an estimate of the surface free energy of adsorption, which is a measure of the strength of these cell-surface interactions.

COLL 311

Highly reproducible and eco-friendly synthesis and characterization of silver nanocrystals and their potential anticancer therapeutic properties

Diana Lomeli-Marroquin, Raúl Rangel-López, Alfonso Nieto Arguello, ponchonieto01@gmail.com, Diana Zárate-Triviño, Jorge L. Cholula-Díaz. Tec de Monterrey, Monterrey, Nuevo Leon, Mexico

Noble metallic nanoparticles, such as silver nanoparticles (Ag-NPs) have been widely studied during the last years, mainly due to their excellent antibacterial properties, beside their potential applications in anticancer treatments. In this work, we report a general procedure to prepare highly reproducible and eco-friendly synthesis of Ag-NPs using potato starch as reducing and stabilizing agent, and water as the solvent. Furthermore, the potential anticancer properties of the synthesized nanostructure was evaluated on MDA-MB and SKBR3, i.e., breast cancer cell lines. The optical properties of the nanomaterials were characterized by UV-visible (wavelength of the maximum absorbance $\lambda_{\max} = 405 \pm 3$ nm for Ag-NPs), whereas the stability of the colloids was analyzed by measuring their Zeta potential, parallel to these studies the colloids showed a stability in dispersion from more than 140 days. The structural properties were determined by X-ray diffraction (XRD), which confirms that the nanostructure possess a Face-Centered Cubic (fcc) crystal structure. The shape and morphology of the nanocrystal were studied by high-resolution transmission electron microscopy (HRTEM) and dynamic light scattering (DLS). The morphology of the nanoparticles were mainly spherical, whereas the size of the nanoparticles were 15 ± 2 nm for Ag-NPs. The yellowish silver colloids showed a cell viability around 75 to 85% on peripheral blood mononuclear cell (PBMC) after 24 h exposure determined by MTT assay using $[AgNPs] = 25200 \mu M$. The evaluation of the cytotoxic of the AgNPs colloids on the breast cancer cell lines, determined also by MTT assay, showed a cell death induction of approximately 80% and up to 90% on MDA-MB and SKBR3, respectively, after 24 h treatment with metallic nanoparticles. Finally, we plan as future study, the green synthesis of gold and bimetallic Ag/Au colloidal nanostructures for potential nanomedicine applications.

COLL 312

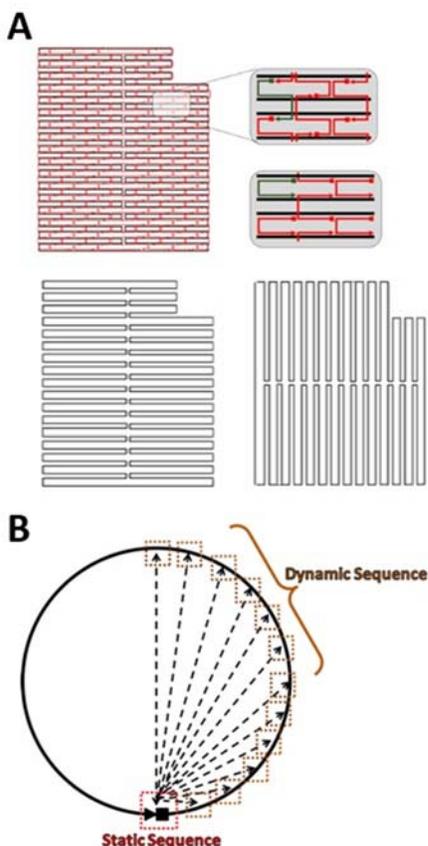
Thermodynamics of DNA looping for origami folding

Jacob M. Majikes, jacobmajikes@gmail.com, Daniel Schiffels, Michael Zwolak, Samuel P. Forry, J. A. Liddle. National Institute of Science and Technology, Gaithersburg, Maryland, United States

Structural DNA nanotechnology uses the last century's strides in biochemical research and commercial DNA synthesis to address nanoscale engineering, physics, and biological challenges. One such technique, DNA origami, has recently shown viability for milligram scale synthesis of nanoparticles. Despite increasing strides towards commercial viability, the impacts of design and processing of DNA based nanostructures are not well understood. This is additionally troublesome as the design of DNA origami presents a plethora of choices to create similar, or identical, structures with little information regarding the impact of these choices on the resulting nanostructures.

The entropic costs associated with large scale looping can play a key role in the folding of DNA origami, both at thermal equilibrium and when kinetics dominate folding. Rigorously understanding how scaffold topology changes impact hybridization thermodynamics and kinetics is therefore worth study. A primitive scaffold system is used to examine thermodynamics via melt curves, leveraging the high throughput of RT-PCR equipment.

Varying the persistence length and folding distance of this primitive, single fold origami will provide insight into the relative impact of topology changes as compared to other facets of origami design such as local GC content or staple length. In addition, this system will be modified to study the impact of molecular crowding. Future work, including kinetics experiments and orthogonal measurements using nanoDSC will provide further insights into origami folding.



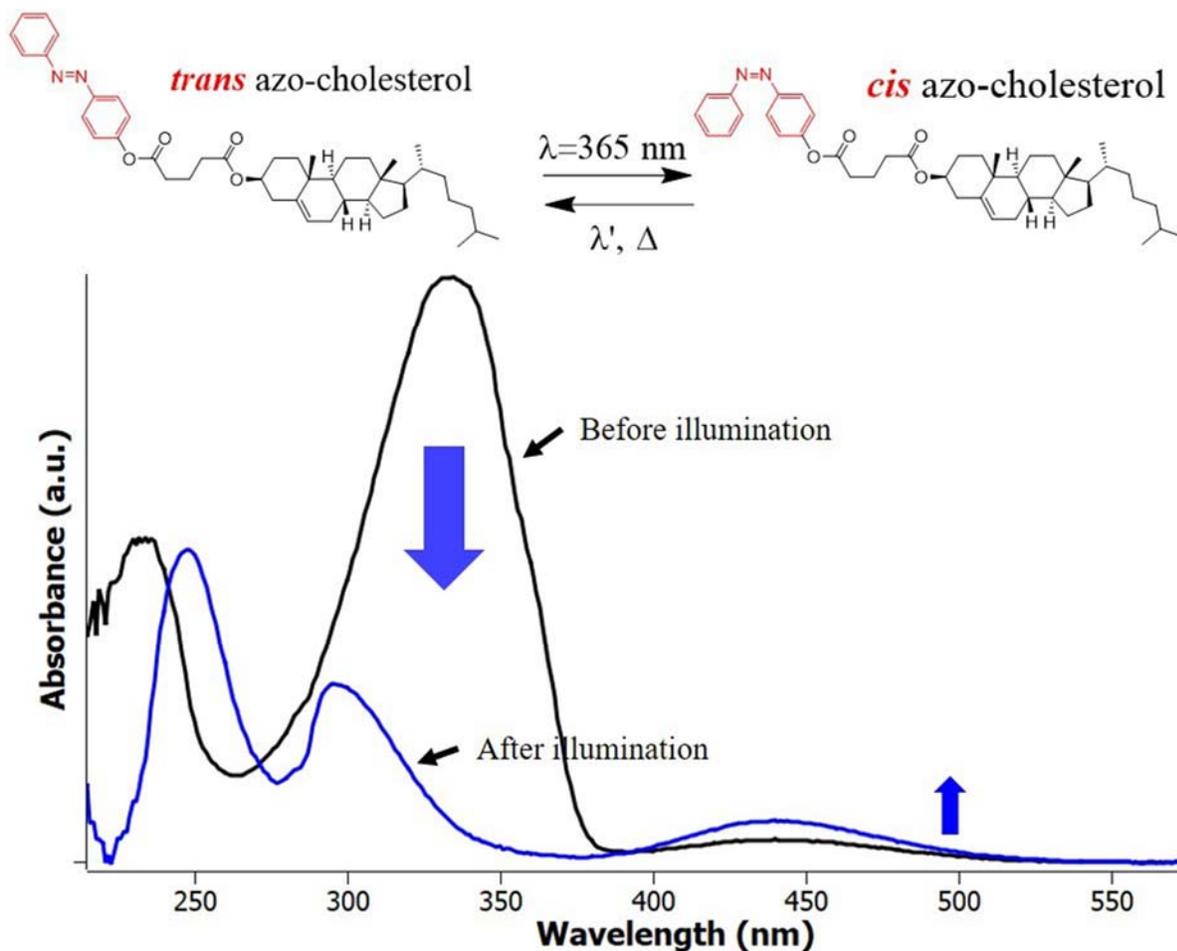
A - DNA origami design examples, staple motif (top), scaffold routing (bottom), B - primitive origami scaffold system

COLL 313

Tuning properties of a family of azo-cholesterol liquid crystals for application as photo-controllable reaction media

Victoria Chang, victoria.chang2@mail.mcgill.ca, Chao-Jun Li, Christopher J. Barrett. Chemistry, McGill University, Montreal, Quebec, Canada

We have developed a system of dimesogens containing azobenzene linked with cholesterol which have unique properties including as liquid crystals with the capacity for photo-control of alignment and order. Photo-control of the order of the medium comes from the *trans-cis* photoisomerization of the azobenzene moiety. By changing the electron donating or withdrawing character of the functional group on the azobenzene moiety and/or the bridging linker between the azobenzene and cholesterol (an ester or a diester with a varying alkyl chain length), it is possible to adjust the photoisomerization wavelength, half-life of the *cis*-azobenzene state, transition temperatures, and structure of this system. These properties have been studied with various characterization methods, including DSC, optical microscope, UV-Visible absorbance, kinetics studies, and NMR. The resulting azobenzene-cholesterol system has an increased level of order compared with isotropic liquids and can be applied as a structured, adaptable, photo-controllable medium for compatible reactions.



Trans-Cis Photoisomerization of Azo-Cholesterol, Absorption Spectra of Azo-Cholesterol Before and After Illumination With Light at 365 nm

COLL 314

Tuning the surface architecture of silver nanoparticles for use as anti-viral agents

Henry Wu¹, wuhen@pdx.edu, **Diana Demchenko**², **Kenneth M. Stedman**², **Marilyn R. Mackiewicz**¹. (1) Chemistry, Portland State University, Beaverton, Oregon, United States (2) Biology, Portland State University, Portland, Oregon, United States

The world population faces a major problem of viral infections that are difficult to treat and, in some cases, cause substantial causes of disease and mortality. While some viral diseases, such as smallpox, have been eradicated with the help of vaccines there are still many pressing viral pathogens that require attention. These viruses include HIV, Rhinovirus, Hepatitis C, Influenza, Zika virus, Yellow fever, Ebolavirus, etc. While tremendous strides have been made with small molecule therapeutic strategies, these drugs are unable to prevent all viral disease and many viruses have already developed resistance to these molecules. Consequently, there is a great need for broad-spectrum antiviral agents against a range of viruses. The tremendous success of silver nanoparticles (AgNPs) as antimicrobial agents in a number of commercially available products has led to an emerging interest in the use of metal nanomaterials as novel antivirals. While recent studies show that AgNPs with various surface coatings can reduce the infectivity of different types of viruses, very little work has been done in this area. Moreover, the mechanisms of viral inhibition of AgNPs is not well understood. Here we will discuss the design of AgNPs with several surface coatings against the viral activity of a robust thermoacidophilic virus *Sulfolobus* spindle-shaped virus (SSV1) and the yellow fever virus. We will evaluate the effect on viral infectivity and the mechanism of inhibition of AgNPs with coatings of polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), sodium citrate, and hybrid lipid membranes. These studies will provide valuable information on the effect of coatings on viral infectivity and we will be able to compare the importance of AgNPs and Ag⁺ ions on viral activity compared to its surface coatings.

COLL 315

Ullmann-like surface reactions and self-assembly of dibromobenzenes and dibromo-bithiophenes

Margaret Wolf, margaret.wolf@uconn.edu, **Rebecca Quardokus**. Chemistry, University of Connecticut, Wethersfield, Connecticut, United States

The push for next generation electronics to be smaller and more efficient has created an increased interest in covalent networks and monolayer surfaces. These materials have the potential to be as thin as one atom while still having the ability to carry current with little resistance. These two-dimensional templates also serve as a base for more intricate functional surfaces. Self assembly is a common method in the development of low-dimensional materials due to ease of preparation. Combining self assembly with the Ullmann surface reaction, a synthetic technique used to couple aryl halides via copper catalysis, can provide more control over the synthesis of these surfaces. We use LT-

UHV scanning tunneling microscopy to study covalent networks of dibromobenzene mixed-monolayer systems on Au(111) created through self-assembly and Ullmann-like coupling. Future experiments will include tip-induced molecular manipulation and reactions, which can aid in the formation of new bonds and specific atomic patterns and arrangements.

COLL 316

Ultrathin PdCu alloy nanosheets for highly efficient electrocatalytic formic acid oxidation

Hongfei Cheng, hcheng009@e.ntu.edu.sg, Nailiang Yang, Hua Zhang. School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

Ultrathin 2D nanomaterials have drawn increasing research attention owing to their relatively high surface area-to-volume ratio and high density of exposed atoms on the surface, which are very advantageous for catalytic reactions. Previous study has shown that Pd electrocatalysts are good candidates for formic acid oxidation (FAO), especially Pd nanosheets. However, the wide application of Pd electrocatalysts toward the FAO is limited by their high cost and low reserve in the earth. To decrease the cost of Pd-based electrocatalysts and further increase their catalytic performance, alloying Pd with earth-abundant materials is an effective strategy. Moreover, in the FAO, Cu is used to improve the catalytic performance and enhance the poisoning tolerance to intermediates, especially CO. Herein, a facile wet-chemical method is reported for the high-yield synthesis of ultrathin PdCu alloy nanosheets under mild conditions. Impressively, the obtained PdCu alloy nanosheet after being treated with ethylenediamine can be used as a highly efficient electrocatalyst for formic acid oxidation. The study implicates that the rational design and controlled synthesis of an ultrathin 2D noble metal alloy may open up new opportunities for enhancing catalytic activities of noble metal nanostructures.

COLL 317

Understanding nanoparticle growth mechanism with liquid cell TEM and computational analysis

Joodeok Kim¹, juori22@gmail.com, Byung Hyo Kim², Jungwon Park¹. (1) School of Chemical and Biological engineering, Seoul National University, Seoul, Korea (the Republic of) (2) Institute for Basic Science, Seoul, Korea (the Republic of)

Understanding nanoparticle growth mechanism is important for the controlled synthesis of nanoparticle. Traditionally, the growth mechanism has been revealed by tracing of sample aliquots, but such ex situ methods cannot provide real time information. Liquid cell TEM make it possible to observe nanoparticle growth directly in sub-nanometer scale. However, analyzing the massive data obtained from in-situ liquid phase TEM to

extract mechanistic understanding in ensemble level is highly challenging and may require computational assistance. Herein, we introduce our study on monitoring real-time synthesis of platinum nanoparticles by using in-situ liquid phase TEM. The time-series of TEM images is converted to binary images and evaluated to track size changes of individual particles using the computational algorithm developed by our group. We show thermodynamic and kinetic factors that govern the particle growth rate and size based on investigating ensemble growth trajectories.

COLL 318

Understanding surface-mediated, emergent plasmonic properties of degenerately doped Cu_{2-x}Se semiconductor nanoparticles

*Xing Yee Gan*¹, *xig39@pitt.edu*, *Lauren Marbella*^{2,1}, *Derrick Kaseman*³, *Jill Millstone*¹. (1) *Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States* (2) *University of Cambridge, Cambridge, United Kingdom*

The phenomena of localized surface plasmon resonances (LSPRs) has been broadly studied and is a property of nanomaterials that can be used to enhance or enable a wide variety of technologies including cancer treatment, light-driven catalysis, and ultrasensitive detection. While most widely observed and studied in noble metal nanomaterials, a much broader selection of nanoscale materials may exhibit LSPRs. Recently, degenerately doped colloidal semiconductor nanoparticles have been identified as one such class of alternative plasmonic nanomaterials. Unlike their noble metal counterparts, a powerful way to tune plasmonic properties of doped semiconductor nanoparticles is by controlling their charge carrier density. Therefore, methods to control and measure carrier density in these materials is crucial to their development and design. Both extrinsic and intrinsic particle features may be manipulated to alter carrier densities, and the resulting concentrations are typically measured using a Drude model interpretation of the particle extinction spectrum. Here, we track and quantify carrier density in a well-studied non-noble metal plasmonic system, copper selenide (Cu_{2-x}Se), using ^{77}Se solid state NMR spin lattice relaxation measurements as a function of particle oxidation. Importantly, we find that ^{77}Se NMR spectroscopy is a sensitive technique able to identify and measure carrier density in Cu_{2-x}Se systems that are metallic, but that do not yet show optically discernable plasmonic features. Further, ^{77}Se NMR simultaneously provides critical information about the structural evolution of these particles as a function of progressive oxidation. We then specifically study surface chemistry-dependent LSPR behaviors in these nanoparticles parsing the impacts of ligand binding motifs from nanoparticle dielectric environment.

COLL 319

Viscosity and surface tension effects on metal sputtered onto low vapor pressure liquids

Mark M. De Luna, mmdeluna@usc.edu, Malancha Gupta. University of Southern California, Los Angeles, California, United States

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications in optics, electronics, and catalysis.

COLL 320

Water interaction with NiFe-based oxide films on Pt(111)/Al₂O₃(0001)

Esther Carrasco¹, esther.carrasco@imdea.org, Miguel A. Niño¹, Paolo Perna¹, Julio Camarero^{1,2}, David Ecija¹, Rodolfo Miranda^{1,2}. (1) Surface Science, IMDEA Nanoscience, Madrid, Madrid, Spain (2) Física de la Materia Condensada, Universidad Autónoma de Madrid, Madrid, Madrid, Spain

Ni-Fe oxides are particularly promising electrocatalysts in alkaline conditions for driving the oxygen evolution reaction (OER) in the splitting of water. Among them, the mixed oxides with 10-50 atomic percentage of Fe present the higher intrinsic activity. In spite of important experimental and theoretical efforts the role of Fe is not fully clarified, and a deeper understanding of the active structure and the oxidation states of Ni and Fe in the active state is still controversial.

In this contribution we present a model Ni-Fe catalytic system which has been prepared according to the surface science methodology. The model system is a layered material consisting of an Al₂O₃(0001) substrate, a buffer layer of a crystalline Pt(111) film deposited by dc magnetron sputtering and a epitaxial thin permalloy film Ni_{0.81}Fe_{0.19}(111) of 1-2 nanometers deposited by molecular beam epitaxy in ultra-high-vacuum conditions and oxidized at different sample temperatures and O₂ doses. The employed procedure allowed to fabricate a set of ultra-thin Ni-Fe catalysts with an ordered surface structure, with different thicknesses and oxidation states of the metallic elements and with a ~19% Fe in the own structure of the catalysts, which is adequate for the OER. The prepared catalysts have been analyzed by X-ray photoelectron spectroscopy, mass spectrometry and low energy electron diffraction before and after exposures to D₂O at room temperature. At increasing water exposures, a progressive surface hydroxylation is induced. A comparison of the as-prepared surfaces and their

chemical transformations upon D₂O adsorption for the different catalysts will be discussed. Preliminary experimental results in combination with near-UV illumination and with electrical charge polarization of the sample, in order to approach the OER conditions, will be shown.

COLL 321

Measurement of *Escherichia coli* using hemoglobin-capped fluorescent gold nanoclusters

Shih-Hua Tan², b812105028@tmu.edu.tw, **Xi-Yu Pan**¹, **Jui Chi Kuo**², **Ting-Kuang Chang**², **Kuan Chen**², **Tsung-Rong Kuo**¹. (1) Graduate Institute of Nanomedicine and Medical Engineering, College of Biomedical Engineering, Taipei Medical University, Taipei city, Taiwan (2) School of Biomedical Engineering, College of Biomedical Engineering, Taipei Medical University, Taipei city, Taiwan

The detection of *Escherichia coli* (*E. coli*) is important for water quality monitoring and food hygiene. Gold nanoclusters (AuNCs) have been widely used in biosensing and bioimaging due to their excellent biocompatibility, stable chemical structure and easy surface modification. In this study, we developed a facile strategy for rapid detection of *E. coli* by using hemoglobin-capped AuNCs (hemoglobin-AuNCs) as their nutrient sources instead of lysogeny broth. After incubation with *E. coli*, the hemoglobin-AuNCs were decomposed because *E. coli* needed to uptake iron ion (Fe³⁺) in order to maintain their metabolism. By the time *E. coli* metabolized hemoglobin on the surface of hemoglobin-AuNCs, fluorescence intensity of hemoglobin-AuNCs was decreased, and then we can calculate the number of *E. coli* in the sample by measuring the OD₆₀₀.

COLL 322

Geometric and optical transformation of a supramolecular host-guest amphiphile

Cynthia Lo, lo.t.cynthia@gmail.com, **Jia Tian**, **William Lindemann**, **Julia Ortony**. Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

We exploit molecular self-assembly of amphiphilic push-pull chromophores to create uniform nanostructures in water. The constituent amphiphilic chromophores were designed to form non-covalent, host-guest complexes with a cyclic host molecule. Upon addition of the host, the chromophore assemblies undergo a geometric and optical transformation. This system represents the first example of molecular self-assembly coupled with host-guest chemistry. Here, we present the synthetic route to our amphiphilic guest molecule, in addition to the nanostructural characterization by TEM, SAXS, and DLS. We use spectroscopic methods to measure optical switching, and demonstrate that this new platform offers unique photochemical and nanostructural properties.

COLL 323

2D materials confined water

Qiang Li, *qiang@sdu.edu.cn. Shandong University, Jinan, China*

The interfaces between water and solid are of fundamental importance owing to its relevance to many physicochemical phenomena and interfacial processes. Although many studies have contributed to a rapid progression in understanding of water/solid interfaces, the exact structure and dynamic behavior of the interfacial water adlayers at ambient conditions is still unclear and many findings and theories are still under debate. Therefore, it will be extremely important to study the structure of water molecules at solid interface or confined between two solid surfaces under molecular level. By utilizing *in situ* thermally controlled AFM, with the assistance of graphene, we have investigated the structure and dynamic behaviors of water adlayers confined in graphene/ mica interface under ambient conditions. Ice-like water adlayers and fluid-like water adlayers have been identified. For the first time, ice-like water adlayers stacked on top of each other up to three layers and the transition from layers to liquid droplets was directly visualized. These new findings of water adlayers growth at the interface will further our understanding of water behaviors at interface.

COLL 324

Laser pulse induced growth of unaggregated Sub-5 nm metal nanoparticles in free-standing graphene films

Yong Yang¹, *kyyoung@umd.edu*, **Dylan J. Kline**¹, **Pankaj Ghildiyal**², **Michael R. Zachariah**^{1,2}. (1) *Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland, United States* (2) *Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States*

Metal nanoparticles with a diameter less than 5 nm have been of great interest because of their unique size- and shape-dependent properties. Manufacturing these metal nanoparticles in an efficient manner, however, is still challenging due to their high non-stability and rapid agglomeration. Here, we report on a rapid laser pulse-induced growth method to *in situ* synthesize well-dispersed NPs within self-standing graphene thin films using metal salt precursors. The rapid heating provided by the laser pulse triggers nucleation and growth of metal nanoparticles in the graphene matrix, and the subsequent rapid quenching freezes these metal nanoparticles in the structure. The role of the duration as well as the power of the laser on the resulting size and morphology is discussed. We find that a shorter laser pulse produces smaller nanoparticles with a narrower size distribution, and that nanoparticle size increases with laser power. Finally, we note that this laser pulse induced growth method could enable scale-up through a roll-to-roll manufacturing process.

COLL 325

Mechanism of osteocalcin interactions with hydroxyapatite surfaces and hydrogen phosphate precursors for bone mineralization

Mahdi Tavakol¹, Samuel Edmund Hoff², samuel.hoff@colorado.edu, Juan Liu¹, Hendrik Heinz³. (1) Colorado University of Boulder, Boulder, Colorado, United States (3) Dept of Polymer Engineering, University of Akron, Akron, Ohio, United States

The mechanism of apatite mineralization mediated by osteocalcin, one of the non-collagenous proteins in bone and dentin, has only been marginally explored due to limitations in experimental imaging and spectroscopy techniques. Recent developments of computational models in the Interface force field (IFF) allow the precise atomically resolved study of the interaction of proteins with hydroxyapatite (HAp) and related minerals using molecular dynamics simulations, including accurate representations of chemical bonding and aqueous interfacial properties as a function of pH value. First, the interaction of osteocalcin with different (hkl) surfaces of HAp facets at pH values of 5, 7 and 10 is discussed and binding residues are identified. In contrast to the proposed role of the three surface-bound calcium ions of the protein as binding sites to hydroxyapatite, these surface-bound ions on the protein are not preferred interaction sites with the HAp surface. Instead, desorbed phosphate ions from the HAp surface, or other hydrogenphosphate precursor molecules in solution, coordinate with the three-calcium site of the protein. Therefore, it appears possible that this site of the protein assumes a prominent role in osteocalcin-mediated biomineralization. The results from molecular dynamics simulation strongly suggest that the three-calcium site of the protein acts as a nucleation site for apatite biomineralization. The hypothesis is in agreement with the prior findings on the proportionality between the number of bone grains and the amount of osteocalcin protein in blood. Revealing the role of osteocalcin in the biomineralization at the atomically resolved level is a significant step towards understanding the process of the bone mineralization, and illustrates the predictive capabilities of simulations using reliable force fields and surface model databases.

COLL 326

Modulation of mechanical properties of organic cocrystals and crystal designing: Impacts of isostructural and polymorphic functional groups

Kamal K. Ray¹, kamalkanti-ray@uiowa.edu, Shalisa M. Oburn¹, Kristin M. Hutchins¹, Thilini P. Rupasinghe¹, Dale C. Swenson¹, Len MacGillivray², Alexei V. Tivanski³. (1) Chemistry, University of Iowa, Iowa City, Iowa, United States (2) Chem Dept, University of Iowa, Iowa City, Iowa, United States (3) Chemistry, The University of Iowa, Iowa City, Iowa, United States

Modulation of supramolecular construction of organic crystals with desirable and controllable electrical, mechanical and optical properties is the central aim of crystal engineering. In particular, modulation of the mechanical properties are crucial for proper

designing and better tableability of active pharmaceutical ingredients (APIs). In this context, inclusion of organic functional groups in the API can modulate the physical and chemical properties of the organic cocrystals. Previously, we have reported that the impact of mechanical properties within organic cocrystal assemblies due to atomic variation, where macro-dimensional crystals showed a lower Young's modulus (YM) as compared to nano-dimensional cocrystals. Herein, we have studied the mechanical properties of cocrystals based on salicylic acid (SA) combined with bipyridine CCFs that contain alkane or alkene functional groups. The selected CCFs were 1,2-bis(4-pyridyl)ethylene (4,4'-BPE) and 1,2-bis(4-pyridyl)ethane (4,4'-BPEth). The resulting 2(SA)(4,4'-BPE) cocrystals exhibit two polymorphs (Form I and II), with the Form-II polymorph being isostructural with the 2(SA)(4,4'-BPEth) cocrystal. Characterizations of YM values of macro- and nano-dimensional cocrystals were performed using atomic force microscopy (AFM). The current study shows that all of the nano-dimensional cocrystals exhibit lower YM values than macro-dimensional cocrystals. Our observations demonstrate that both nano-dimension and macro-dimension cocrystals of the two isostructural cocrystals can be differentiated based on separate YM values. The YM values of 2(SA)(4,4'-BPE) cocrystals are nearly half compared to isostructural 2(SA)(4,4'-BPEth). Moreover, we managed to distinguish between the two polymorphs of 2(SA)(4,4'-BPE) by their distinctive YMs, where Form I exhibits a 70% increase in YM compared to Form II. Overall, we expect our study to help design, and better understand, structure-property relationships of pharmaceutical cocrystals.

COLL 327

Fabrication of monodisperse polymerc microparticles coated with silica through droplet based microfluidic system

Dong-Yeong Kim, dongyeong4402@gmail.com, Si Hyung Jin, Seong-Geun Jeong, Byungin Lee, Kyoung-Ku Kang, Chang-Soo Lee. Chemical Engineering and Applied Chemistry, Chungnam national university, Daejeon, Korea (the Republic of)

Recently, attention of silica coated polymer particle has been an increasing interest, because of their development possibility of applications in catalyst, coating, and drug delivery. The synthesis of organic-inorganic hybrid particles with highly controlled particle sizes in the micrometer range is a major challenge in many areas of research. In this work, we demonstrate a novel and facile droplet based microfluidic method for preparation of hybrid microparticles coated with silica nanoparticles. In this approach, the droplet-based microfluidic method combined with in situ photopolymerization produces highly monodisperse silanol groups functionalized organic microparticles in a simple manner, and the silica nanoparticles gradually grow on the surface of the microparticles prepared via hydrolysis and condensation of tetraethoxysilane (TEOS) in a basic ammonium hydroxide medium without additional surface treatment. This approach leads to a reduction in the number of processes and allows drastically improved size uniformity compared to conventional methods. The morphology, composition, and structure of the hybrid microparticles are analyzed by SEM, TEM, FT-IR, EDS, and XPS, respectively. As a result, Organic core of hybrid particles is

completely covered with the silica nanoparticles of approximately 60nm. Finally, based on the observation of the growth of the silica nanoparticles on the surface of the organic core particles, we describe the formation mechanism of a silica inorganic shell.

COLL 328

Surface-ligand effect on radiosensitization of ultrasmall luminescent gold nanoparticles

Xingya Jiang, jxy19920402@gmail.com. Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States

Gold nanoparticles (AuNPs) could serve as potential radiotherapy sensitizers because of their exceptional biocompatibility and high-Z material nature; however, since in vitro and in vivo behaviors of AuNPs are determined not only by their particle size but also by their surface chemistries, whether surface ligands can affect their radiosensitization has seldom been investigated in the radiosensitization of AuNPs. By conducting head-to-head comparison on radiosensitization of two kinds of ultrasmall (~2nm) near-infrared (NIR) emitting AuNPs that are coated with zwitterionic glutathione and neutral polyethylene glycol (PEG) ligands, respectively, we found that zwitterionic glutathione coated AuNPs (GS-AuNPs) can reduce survival rates of MCF-7 cells under irradiation of clinically used megavoltage photon beam at low dosage of ~2.25Gy. On the other hand, PEG-AuNPs can serve as a radiation-protecting agent and enabled MCF-7 cells more resistant to the irradiation, clearly indicating the key role of surface chemistry in radiosensitization of AuNPs. More detailed studies suggested that such difference was independent of cellular uptake and its efficiency but might be related to the ligand-induced difference in photoelectron generation and/or interactions between AuNPs and X-ray triggered ROS (reactive oxygen species).

COLL 329

Using atomic force microscopy to evaluate ligand-mediated stabilization of EGaIn liquid metal nanoparticles

Syeda S. Akhter, syeda.akhter001@umb.edu, Khosrow Dinyaryan, Michelle C. Foster. Chemistry, University of Massachusetts Boston, Boston, Massachusetts, United States

Nanoparticles containing a eutectic gallium indium (EGaIn) liquid-metal core with a polymeric outer shell have potential as nanocarriers in drug delivery systems. EGaIn nanoparticles are created using fluidic shearing and have diameters that range from 6.4 nm to >10 μ m. The particles have a passivating layer of gallium oxide (Ga_2O_3) on their surface. This oxide layer will bind to different kinds of organic ligands such as aliphatic carboxylic acids creating functional nanocomposite platforms which has high potential in healthcare and biomedical applications. Changing the length of the hydrocarbon chain in the aliphatic acids will have effect on size and yield of EGaIn nanoparticles formation.

Atomic force microscopy (AFM), a novel analytical technique, can reveal the detailed surface characteristics of these ligand coated nanoparticles. AFM phase images will provide information beyond topography including identifying ligand coverage and their distribution upon the particles. AFM force-curve analysis will provide information on mechanical properties of the surface such as adhesive behavior of the coating, coating thickness, elasticity, etc. Understanding fundamental surface chemistry of the ligand-nanoparticle interface is crucial for evaluating efficiency of these ligand mediated nanoparticles in medical engineering application. This talk describes our studies on morphological and mechanical properties of EGaIn particles coated with different kinds of aliphatic carboxylic acids varying the chain length that will evaluate the efficiency of these nanoparticles.

COLL 330

Room-temperature ionic liquid based nanoemulsions: Synthesis and formulation for delivery of poorly water soluble active pharmaceutical agents

*Moira M. Esson*¹, esson@wisc.edu, *Sandro Mecozzi*^{1,2}. (1) Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States (2) Pharmacy, University of Wisconsin-Madison, Madison, Wisconsin, United States

Amphotericin B (AmB) is a highly effective polyene antifungal agent typically used for invasive fungal infections. Despite the efficacy of this drug, there are major limitations to its use due to adverse side effects, including acute infusion-related febrile reactions and dose-dependent nephrotoxicity. These effects are attributed, at least in part, to the aggregation of AmB due to its extremely poor water solubility. To overcome this problem, we have designed a novel drug delivery system that harnesses the unique properties of ionic liquids. Ionic liquids are organic cations and anions whose melting point is below 100°C; some of which are remarkably liquid at room temperature. Here, high concentrations of AmB were solubilized in a hydrophilic cholinium-based room temperature ionic liquid, a novel hydrophobic dicationic cholinium-based ionic liquid, and in mixtures of the two. The absorption spectrum of AmB in the ionic liquid, ionic liquid mixtures, and prepared nanoemulsion indicates excellent monomerization. *In vivo* biocompatibility of the ionic liquids was analyzed using zebra-fish assays and the novel dicationic cholinium-based ionic liquid was characterized using differential scanning calorimetry (DSC). The relative hydrophobicity of the prepared ionic liquids was analyzed using pyrene fluorescence studies. Nanoemulsions of the ionic liquids and ionic liquid mixtures were prepared and *in vitro* biocompatibility was analyzed using a cell viability assay. Hemolytic activity of the AmB ionic liquid nanoemulsion was analyzed and the antifungal activity of the AmB nanoemulsion formulation was evaluated against *Candida Albicans*.

COLL 331

Mechanically tunable inter-bonding, assembly and macrostructures of nanoparticles in biominerals

Z R. Tian^{1,2}, rtian@uark.edu, Licheng Hua^{2,3}. (1) Chemistry/Biochemistry, University of Arkansas, Fayetteville, Arkansas, United States (2) Institute for Nanoscience/Engineering, University of Arkansas, Fayetteville, Arkansas, United States (3) Mechanical Engineering and Mechanics, Ningbo University, Ningbo City, Zhejiang Province, China

The enormous progress to date in the controlled nanosyntheses of different nanomaterials has naturally called for the development of new methods for constructing the nanomaterials into three-dimensional (3D) functional macrostructures, which stimulates us to understand, measure and control the bonding between 0D- and 1D-nanoparticles large and small. Here we report a new study on the self-assembled nanocrystals in both mammal teeth enamel and seashells by means of the X-ray diffraction (XRD), scanning electron microscope (SEM), and atomic force microscope (AFM). The self-assembly bonding energy long-unmeasurable thermodynamically has been measured mechanically. Thus-based mechanonanochemistry has complemented the classic chemical thermodynamics, and further revealed that the nanoparticles' inter-bonding and structural 3D-assembling in the biominerals are mechanically tunable at ambient temperature and pressure on demand. This new branch of the nanochemistry can help not only produce new materials from fine nanoparticles by design at ultralow-cost in future, but also develop new treatments to protect the teeth from the dehydration damage for patients of all walks with the dry mouth syndrome.

COLL 332

Development of novel nanostructured pharmaceuticals to enhance solubility and overall biological performance

Richard V. Jones¹, richard.jones@thalesnano.com, Eniko Manek¹, Ferenc Darvas^{1,2}. (1) InnoStudio, Budapest, Hungary (2) FIU, Miami, Florida, United States

Nanotechnology provides new innovative solutions for original as well as generic applications in a wide variety of industries including pharmaceuticals, agrochemicals, cosmetics, foods, nutraceuticals and home care. This technology has led to the creation of nano-formulated drugs, which have unique supramolecular structures with improved clinical utility such as increased exposure, reduced or eliminated food effect, changed administration route.

The novel supramolecular structures can deliver substantial improvements in material properties and biological performances, such as:

1. Solution like behaviour that ensures optimal systemic exposure;
2. Substantial increase in apparent solubility facilitating the compound availability of absorption;
3. Unique absorption mechanism that does not require traditional dissolution processes and results in improved drug absorption.

Using novel bottom-up nanoparticle pharmaceutical delivery technology, called SpeedyNano™, that relies on controlled continuous-flow precipitation, we have prepared several unique nanostructured pharma delivery systems. The properties of the produced nanostructured particles could be modified during the process by the precise control and optimization of various reaction parameters (e.g. temperature, flow rate, pH and concentration).

Using examples of nano-formulating indomethacin, rosuvastatin, and zanamivir, as well as antibiotics we will demonstrate in this presentation how we could substantially improve their biological activities.

COLL 333

Comparing macrocycle assembly at surfaces and in solution: 2D stacking and 3D packing

Henry D. Castillo, henrcast@indiana.edu, John M. Espinosa Duran, James Dobscha, Sibali Debnath, Jing Yang, Yuriy Sereda, Krishnan Raghavachari, Amar H. Flood, Peter Ortoleva, Steven L. Tait. Department of Chemistry, Indiana University, Bloomington, Indiana, United States

Small molecule self-assembly offers an efficient route to highly-ordered organic materials that can be programmed with for a variety of chemical and electronic applications, including semiconductors, LEDs, and photovoltaics. However, the success of these materials depends on the ability to program intermolecular interactions leading to excellent ordering at the interface to a solid support and then templated stacking into a thin film. These ordering and stacking processes at surfaces can differ significantly from packing in solution. Here, a prototypical molecular platform of tricarbazolo triazolophane macrocycles (tricarb) was designed to incorporate lateral non-traditional hydrogen bonding and co-facial electrostatic interactions between macrocycle cores as well as van der Waals (vdW) interactions between peripheral alkyl chains. Building on this macrocycle framework, we program peripheral alkyl units and solvent interactions to steer self-assembly in solution and at the solution-HOPG interface. We combine scanning tunneling microscopy, electron microscopy, and X-ray scattering with molecular dynamic simulations to understand the self-assembly of these macrocycles. While the 2D assembly features non-traditional hydrogen bonding between adjacent macrocyclic cores, packing can be directed by concentration and alkyl chain length between four different architectures that differ in packing density and hydrogen bonding interactions. Experiments with solvent mixtures show that the transition between each architecture can be altered and 3D growth from the surface can be promoted, depending on the level of solvation. In solution, self-assembly is dependent on vdW interactions and co-facial dipole interactions between macrocycles to form loose hexagonal structures of columns. By combining experiment and theory in this collaborative work, a further understanding was obtained of how intermolecular interactions drive the hierarchical assembly of molecular building blocks into patterned organic materials.

COLL 334

Preparation of fabrics with directional water-transport property

Lihong Lao, ll728@cornell.edu, Dahua Shou, Yuen Shing Wu, Jintu Fan. Cornell University, Ithaca, New York, United States

Clothing provides a microclimate between the body and the external environment, and acts as a barrier for heat and vapor transfer in between. In sweating conditions, in order to maintain the thermal comfort, fabric next to the skin should not only absorb liquid rapidly but also transport it through the fabric promptly to avoid the discomfort of the fabric sticking to the skin. On the other hand, in the raining weather, the fabric next to the environment is desired to prevent the water passing from the environment to the skin, and thus should possess water-resistant or water-proof properties. Therefore, there's a demand to design a fabric material that has an asymmetric wettability and could directionally transport water from the skin to the environment, but minimize the transport in the reverse direction.

In this project, we worked towards this goal — endowing asymmetric wettability on breathable fabrics to enable directional (differential) water transport properties. We used a combination of superhydrophobic finishing and plasma selective treatment to create gradient wettability channels through the fabric thickness. While these channels were served for directional liquid transport, the untreated larger surface remained superhydrophobic, therefore could still provide thermal comfort and water-resistant properties next to the skin and the environment, respectively. The differentiated water transport ability was confirmed by a home-made measurement device. Additionally, SEM, TGA, chemical analysis, and contact angle measurements were performed to determine the surface structure and wettability of the fabric after various modification conditions.

COLL 335

Wax patterning on flexible plastics for biomedical, microfluidic and electrochemical applications

Ahmad Z. Qamar¹, azqamar@siu.edu, Sensen Chen¹, Kshitij Amar², Punit Kohli¹, Farhan Chowdhury², Mohtashim Shamsi¹. (1) Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois, United States (2) Department of Mechanical Engineering and Energy Processes, Southern Illinois University Carbondale, Carbondale, Illinois, United States

Chemical and biochemical processes using miniature devices (lab on a chip) gained lot of attention in last decade. Robust, cost effective and compact devices have always been the attractive features of analytical platforms to save time, money and space. Previously reported methods require to create screen patterns or need trained persons and sophisticated technology to develop miniature devices. Unavailability of trained

personal and clean room facilities limit the mass production of devices. Wax printing has become alternate approach to create customized microfeatures for lab on a chip applications. We are working on printability, fidelity and application of wax micropatterned devices on polyethylene terephthalate (PET). Microchips were designed on Inkscape and printed on PET substrate using solid wax printer. Surface topography and printed widths was investigated by using optical microscope while height of printed wax was measured by SEM. Mouse embryonic stem cell (mESC) self-renewal and direct differentiation could possibly be exemplified on wax patterned microwells. Fluorescence microscopy was used for quantification of self-renewal and differentiation of mESC on Collagen I or Fibronectin coated microwell surfaces. Evolution of microchannels on PET could also be an appealing approach to build microfluidic platforms. The wax microchannels were found heat resistant till 80 °C. 0.25 µL volume of model fluid “simulated urine” was able to run in 100 µm channels. Electrodes were patterned using inkjet printing and wax printing and characterized electrochemically. Their electrochemical response was comparable to commercially available screen-printed electrodes. Cost of inkjet/wax printed device is \$0.03 against cost of screen printed device (\$5.00). Biomedical, microfluidic and electrochemical studies suggest that PET substrates can be used in future to fabricate rapid, economical and high throughput multilayered wax printed devices in combination with inkjet printing to explore more potential applications.

COLL 336

Transitioning to the field: *Operando* effects on chemical warfare agent decontamination with zirconium hydroxide

Robert Balow¹, bobbybalow@gmail.com, Grant C. Daniels¹, Monica L. McEntee², Wesley O. Gordon³, Gregory Peterson², James H. Wynne¹, Pehr E. Pehrsson¹. (1) Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States (2) Edgewood Chemical Biological Center (ECBC), Aberdeen Proving Ground, Maryland, United States (3) Research and Technology Directorate, U. S. Army Edgewood Chemical Biological Center, Belcamp, Maryland, United States

The recent use of toxic chemicals and chemical warfare agents (CWAs) in London, Syria, and Malaysia is a grim reminder of the need for compounds capable of rapidly capturing and decontaminating toxic chemicals and CWAs. Unfortunately, the chemical diversity of CWAs makes finding an all-in-one decontaminant difficult. Furthermore, the impact of atmospheric components such as CO₂, humidity, and vehicle exhaust is relatively unknown. These environmental factors can adsorb to many promising decontamination compounds and may block active sites necessary for CWA decontamination.

The diverse surface chemistry of zirconium hydroxide (Zr(OH)₄) nanoparticles makes it an ideal candidate for broad spectrum decontamination. However, field use of Zr(OH)₄ requires a comprehensive understanding of how environmental components affect the reactivity of Zr(OH)₄. This presentation focuses on the interaction of the

Zr(OH)₄ surface with various operationally-relevant environmental factors. Using a suite of ambient techniques (operando FTIR, GC-MS, etc.), we elucidated how the surrounding environment affects the performance of Zr(OH)₄ with respect to decontamination of a compound chemically similar to Sarin gas.

COLL 337

Quantum mechanical derived description of physical adsorption

James B. Condon^{1,2}, condonj@genchem.net. (1) Chemistry, Roane State - Retired, Kingston, Tennessee, United States (2) IFF, Forschungszentrum Juelich, Juelich, Germany

The quantum mechanical derivation of the physical adsorption isotherm is reviewed and explained. The method starts by making a separation of variables into the direction normal to the surface and parallel to the surface. The normal to the surface is calculated using a Leonard-Jones potential. However, this is not the most important calculation. The wave function in the direction parallel to the surface is model using QM analog of Fuller's Auto-Shielded Physisorption (ASP) model, that is the adsorbed molecules are treated as a perturbation on the surface, which may be treated as a "particle in the box" with a perturbing energy due to other adsorbate molecules. The derived isotherm equation for a non-porous plane surface has a simple form:

$$\theta = \Delta\chi \mathbf{U} \Delta\chi \text{ where } \Delta\chi = \chi - \chi_c, \chi_c = -\ln(E_{\text{ads}}/RT) \text{ and } \chi = -\ln(-\ln(P/P_{\text{vap}}))$$

Where \mathbf{U} is the unit step function and E_{ads} (< 0) is the energy of adsorption for the first adsorbate molecule. For non-porous surfaces with one E_{ads} a plot of n_{ads} , moles adsorbed, versus χ yields the E_{ads} , as the abscissa intercept, and n_m , the monolayer equivalent moles from the slope, since $\theta := n_{\text{ads}}/n_m$. Comparisons to "standard adsorption isotherms" will be presented along with experimental evidence of the threshold pressure predicted by this theory. This latter effect is support by Dubinin's "Thermodynamic criterion" and the isotherms that use this concept, and by the disjoining pressure theory.

Additional implications include: For porous adsorbents and surfaces with more than one E_{ads} the plot's first and second derivative with respect to n_{ads} yields the E_{ads} distributions, and both the micropore and the mesopore dimensions and distributions as well as the external surface area. The expanded theory in terms of two adsorbates has also been successful in determining the binary adsorption phase diagram with a minimum of measurements.

COLL 338

Molecular detection and analysis of exosomes using surface-enhanced Raman scattering gold nanorods and a miniaturized device

Elyahb Allie Kwizera¹, akwizera@memphis.edu, Xiaohua Huang^{2,1}, Ryan T. O'Connor³. (1) Chemistry Department, University of Memphis, Memphis, Tennessee, United States (2) Chemistry, The University of Memphis, Germantown, Tennessee, United States (3) Chemistry, University of Memphis, Griffin, Georgia, United States

Exosomes are 40-200 nm sized vesicles that are shed from every type of cell into an extracellular environment. Recently exosomes have attracted interest due to their potential as cancer biomarkers because they transport molecular contents of the cells from which they originate. Their detection and molecular profiling is technically challenging especially due to their small sizes and environment from which they are found. Here, we report a novel method for exosome detection and protein profiling using Surface Enhanced Raman Scattering (SERS) nanotags in combination with a miniaturized capture platform. A gold-coated glass slide is functionalized with antibodies to enable capture and profiling of exosome surface proteins. We report that exosome derived from breast cancer can be identified by their expression of EpCAM and HER2 biomarkers. This method offers a simple, rapid, highly sensitive Raman based assay for point of care detection and molecular profiling of exosome capable of differentiating different subtypes of cancer cells and able to differentiate cancer cells from normal cells in less than two hours. This next-generation Raman exosome assay has the potential to revolutionize exosome research and realize a novel cancer liquid biopsy approach for cancer research and early detection.

COLL 339

Interfacial structuring of chitosan hydrogel provide enhanced wear protection

Xavier Banquy¹, xbanquy@gmail.com, Jimmy Faivre^{1,2}, Guillaume Sudre², alexandra montembault², stephane benayoun², thierry Delair², Laurent David². (1) University of Montreal, Montreal, Quebec, Canada (2) Universite of Lyon Claude Bernard, Lyon, France

We present the fabrication of chitosan hydrogels exhibiting a bilayered structure. This bilayered structure, as shown by SEM and confocal microscopy, is composed of a thin dense superficial zone (SZ), covering a deeper zone (DZ) containing microchannels orientated perpendicularly to the SZ. We show that such structure favors diffusion of macromolecules within the hydrogel matrix up to a critical pressure, σ_c , above which channels start to collapse. Moreover, we found that the SZ provided a higher wear resistance than the DZ which was severely damaged at a pressure equal to the elastic modulus of the gel. The coefficient of friction (CoF) of the SZ remained independent of the applied load with $\mu_{SZ} = 0.38 \pm 0.02$, while CoF measured at DZ exhibited two regimes: an initial CoF close to the value found on the SZ, and a CoF that decreased to $\mu_{DZ} = 0.18 \pm 0.01$ at pressures higher than the critical pressure σ_c . Overall, our results show that hierarchical structuring is a promising avenue in controlling and improving the wear resistance of soft materials such as hydrogels.

COLL 340

Mussel-inspired cellulose nanocomposite tough hydrogels with synergistic self-healing, adhesive and strain sensitive properties

Changyou Shao, *scy2016@bjfu.edu.cn*, Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, Beijing, China

The remarkable progress in efforts to prepare conductive self-healing hydrogels mimicking human skin's functions has been witnessed in recent years. However, it remains a great challenge to develop an integrated conductive gel combining excellent self-healing and mechanical properties, which is derived from their inherent compromise between the dynamic cross-links for healing and steady cross-links for mechanical strength. In this work, we design a tough, self-healing and self-adhesive ionic gel by constructing synergistic multiple coordination bonds among tannic acid-coated cellulose nanocrystals (TA@CNCs), poly(acrylic acid) chains and metal ions in a covalent polymer network. The incorporated TA@CNC acts as a dynamic connected bridge in the hierarchically porous network mediated by multiple coordination bonds, endowing the ionic gels the superior mechanical performance. Reversible nature of dynamic coordination interactions leads to excellent recovery property as well as reliable mechanical and electrical self-healing property without any assistance of external stimuli. Intriguingly, the ionic gels display durable and repeatable adhesiveness ascribed to the presence of catechol groups from the incorporated tannic acid, which can be adhered directly on human skin without inflammatory response and residual. Additionally, the ionic gels with a great strain sensitivity can be employed as flexible strain sensors to monitor and distinguish both large motions (e.g., joints bending) and subtle motions (e.g. pulse and breath), which enable us to analyze the data on the user interface of smart phone via programmable wireless transmission. This work provides a new prospect for the design of the biocompatible cellulose-based hydrogels with stretchable, self-adhesive, self-healing and strain sensitive properties for potential applications in wearable electronic sensors and healthcare monitoring.

COLL 341

Glycocalyx mimetic surfaces reduce blood protein adsorption and fibrin polymerization

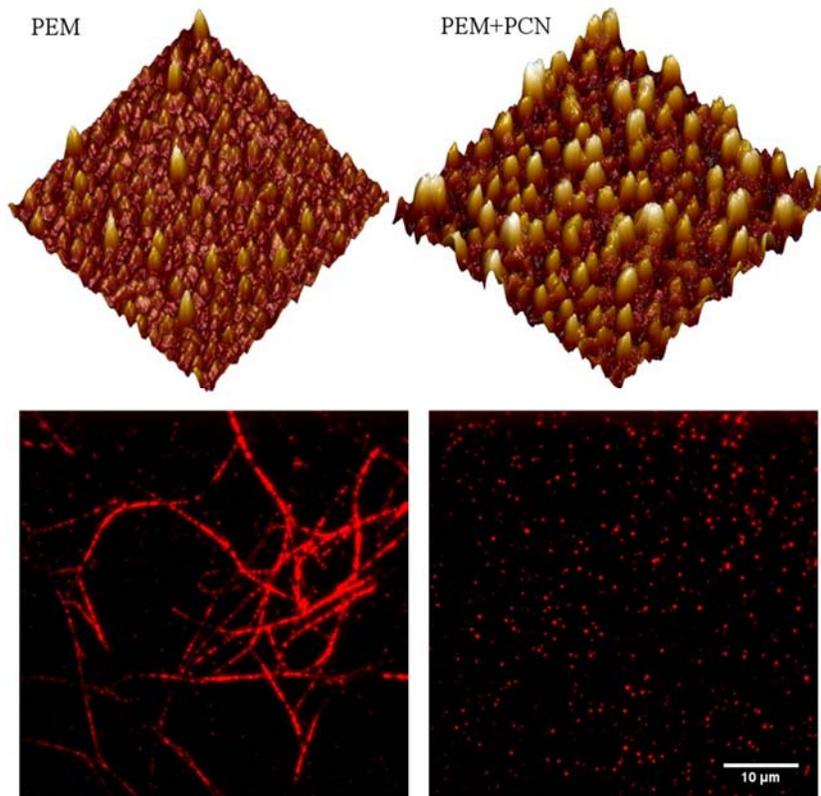
Mohammadhasan Hedayati¹, *hedayati.che@gmail.com*, **Melissa M. Reynolds**², **Diego Krapf**¹, **Matt Kipper**³. (1) Colorado State University, Fort Collins, Colorado, United States (2) Chemistry Department, Colorado State University, Fort Collins, Colorado, United States (3) Dept of Chem Biol Engineering, Colorado State University, Fort Collins, Colorado, United States

Protein adsorption leading to blood clotting is a major problem for the successful performance of blood-contacting biomaterials. When a biomaterial comes into contact with blood it rapidly becomes covered with a layer of adsorbed proteins. This protein

layer may initiate blood clotting by promoting platelet adhesion, activation, and aggregation.

One way to design a blood-compatible biomaterial is to mimic the inside surfaces of blood vessels, where blood does not coagulate. The endothelial glycocalyx, a saccharide-rich layer, containing proteoglycans, glycoproteins, and glycosaminoglycans, covers the luminal surface of the vascular endothelium. We have developed glycocalyx-like surface coatings, by combining layer by layer assembly of polyelectrolyte multi-layers (PEMs) with GAG-rich polyelectrolyte complex nanoparticles (PCNs) (Fig. 1, top) to study how structure and composition modulate protein adsorption.

While the amount of adsorbed blood proteins on the surface of biomaterials is of longstanding fundamental and practical interest, little attention has been paid to interfacial dynamics of proteins on the surface. We have used single-molecule tracking to measure a large number of single protein trajectories ($\sim 10^4$) to explicitly visualize the process of adsorption and desorption of albumin, fibrinogen, and von Willebrand factor, and fibrin polymerization (Fig. 1, bottom) on our model glycocalyx like surfaces. Understanding how to control these interactions through controlling the surface features will enable the rational design of new blood-contacting materials for medical devices and implants.



Synergistic action of hyaluronic acid and lubricin prevents surface adhesion in articular joints

Huijun Ye¹, yehuijun@tju.edu.cn, **Rongxin Su**², **Wren Greene**³, **Renliang Huang**⁴, **Wei Qi**⁵, **Zhimin He**⁶. (1) School of Chemical Engineering and Technology, Tianjin University, Tianjin, Tianjin, China (3) Institute of Frontier Materials, Deakin University, Burwood, Victoria, Australia (4) School of Enviro Science and Eng, Tianjin University, Tianjin, China

As a complex disease, osteoarthritis (OA) is usually initiated with some abnormal components (inflammatory mediators, enzymes and plasma proteins, etc.) existed in synovial fluid reaching the joint surface. Therefore, effectively preventing the adsorption of these components on cartilage surface would play role in the protection of cartilage surface from degradation and avoiding OA disease. Bioinspired by the respective antifouling ability of two intrinsic compositions in synovial fluid and on cartilage surface, that is hyaluronic acid (HA) and lubricin (LUB), we fabricated a composite layer of them on Au (Au-HA/LUB) surfaces and to investigate whether they have synergistic effect on resisting unfavorable attacks. Both the results of surface plasmon resonance (SPR) biosensors and quartz crystal microbalance (QCM) showed that HA together with LUB could synergistically enhance the antiadhesive ability by at least one time than their respective alone, especially for proteins from single solution (2mg/mL), achieving an ultralow fouling level ($< 5 \text{ ng/cm}^2$). We also did some interaction force measurements which further demonstrated the weaker adhesion force and adhesion energy of different functional groups (amino groups, carboxyl groups, and methyl groups, which are typical groups existing in proteins) formed on Au-HA/LUB surfaces than that on Au-HA or Au-LUB surfaces. Our work might provide a novel way to fabricate antifouling surfaces and help better understanding the synergy between HA and LUB on cartilage surfaces.

COLL 343

Enhancing and tuning the lectin binding behavior by functionalization of gold nanoparticles with precision glycomacromolecules

Sophia Boden, sophia.boden@uni-duesseldorf.de, **Kristina Wagner**, **Matthias Karg**, **Laura Hartmann**. *Heinrich-Heine University düsseldorf, Düsseldorf, Germany*

The functionalization of gold nanoparticles with carbohydrate carrying thiolated ligands leads to so-called glyco-gold nanoparticles (glyco-AuNPs). Such glyco-AuNPs are promising candidates for their use in biosensing or as inhibitors of carbohydrate recognizing receptors.

Here, we report the use of solid phase polymer synthesis to obtain precision glycomacromolecules that allow for the functionalization of AuNPs and give access to a variety of glyco-AuNPs with tunable features. Synthesis of the glycomacromolecules is based on the stepwise assembly of tailor-made building blocks on solid support giving monodisperse, sequence-defined oligo(amidoamines) with pendant glycoligands. Thereby, the chemical structure of the glycomacromolecules can be varied

systematically changing e.g. spacing characteristics, valency and overall length of the glycomacromolecule. By the use of L-cysteine as final building block, thiolated precision glycomacromolecules were generated and successfully employed for AuNP functionalization by ligand exchange reaction.

The synthesized glyco-AuNPs exhibit a high degree of functionalization and high stability in buffers of high ionic strength. Applying UV-Vis, DLS and SPR measurements, the binding behavior of differently functionalized glyco-AuNPs to model lectin Concanavalin A was investigated.

Results showed that not only an increase in lectin binding can be achieved by the multivalent presentation on the AuNP surface in comparison to the free ligand but also that binding strength depends on the chemical structure of the ligand such as valency and hydrophobicity. Overall, we demonstrate the modular synthesis of glyco-AuNPs with tunable lectin binding behavior.

COLL 344

Interfacing electron transfer proficient cells with metal surfaces using DNA

Ariel L. Furst, ariel.furst@gmail.com, Matthew B. Francis. University of California, Berkeley, California, United States

Precise control over the interaction between living systems and electroactive surfaces has long been a goal in healthcare and green energy production. A key challenge in the interaction of cells with inorganic surfaces is to maintain specificity in the placement of cells while facilitating electron transfer between the cells and the surface. DNA is unique in its ability to both self-recognize and conduct current. These abilities have enabled its application in a variety of fundamental scientific and medical devices. Through DNA hybridization-based cell adhesion, we have used DNA-modified electrodes to capture and quantify non-adherent mammalian cells, yeast, and microbes. Importantly, we have rapidly assembled low-density monolayers of electron transfer proficient cells that preserve their electron transfer capabilities prior to biofilm formation. We attribute this ability, at least in part, to the conductivity of DNA. We believe this DNA-based technique of interfacing cells with inorganic surfaces will have applications ranging from biofuel cells to diagnostic tools.

COLL 345

Ladderane phospholipids form dense, low-polarity membranes with low proton/hydroxide permeability

Frank R. Moss¹, mossfr@stanford.edu, Steven Shuken¹, Jaron Mercer¹, Carolyn Cohen¹, Thomas Weiss², Noah Z. Burns¹, Steven G. Boxer¹. (1) Department of Chemistry, Stanford University, Stanford, California, United States (2) Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University, Menlo Park, California, United States

Ladderane lipids, with a ladder-like structure of fused cyclobutane rings in their hydrophobic tails, are exclusively found in bacteria that perform anaerobic ammonia oxidation (anammox), suggesting that they play a crucial role in anammox metabolism. As anammox bacteria have not been grown in pure culture and grow extremely slowly in enrichment cultures, researchers have not been able to isolate sufficient quantities of pure ladderane lipids to measure the biophysical properties of ladderane membranes. Without knowledge of the physical properties of ladderane lipids or tools for studying the lipids *in vivo*, their biological functions and potential applications remain unknown. To answer these questions, we have developed efficient total syntheses of naturally occurring ladderane phospholipids and unnatural analogs for full structure-function studies. We show that ladderane lipids have physical properties that are distinct from conventional straight-chain lipids. Ladderane lipids form dense bilayers with slow lateral diffusion and dense monolayers with low compressibility. These physical properties result in membranes with rates of transbilayer proton diffusion that are an order of magnitude slower than for membranes composed of straight-chain phospholipids. As a proton gradient is used to drive ATP synthesis in anammox bacteria, these results suggest that ladderane lipids in the anammoxosome may prevent the dissipation of the proton gradient during the slow anammox metabolism. To explore how ladderane lipids form such impermeable membranes, we use Nile red solvatochromism to show that the hydrophobic interior of ladderane bilayers is highly nonpolar, likely due to a smaller number of water molecules in the bilayer interior. These results provide experimental evidence for the theoretical model of membrane permeability that involves proton conduction through water wires. On the other hand, small ions and molecules appear to diffuse across membranes via a direct partitioning/diffusion mechanism. The synthesis of ladderane lipids has increased the chemical diversity of hydrophobic tail structure in phospholipids available to explore the structure and function of lipid membranes, including ion permeation. Additionally, the physical properties of ladderane membranes may make them useful for reconstituting membrane proteins, creating stable membrane-based sensors, and drug delivery.

COLL 346

Tetrazine ligation-mediated layer-by-layer deposition for the development of antifibrotic patches

He Zhang¹, hezhang@udel.edu, **Anitha Ravikrishnan**¹, **Xinqiao Jia**², **Joseph M. Fox**². (1) *Material Science and Engineering, University of Delaware, Newark, Delaware, United States* (2) *University of Delaware, Newark, Delaware, United States*

Combining electrospinning, layer-by-layer deposition and tetrazine ligation, the inverse-electron-demand Diels-Alder cycloaddition between s-tetrazines (Tz) and trans-cyclooctenes (TCO), we are developing a new type of fibrous patches capable of modulating cellular programs and the extracellular environment to suppress fibrogenesis and to regenerate the normal functions of soft connective tissues. Fibrous scaffolds with an average fiber diameter of 5 μm were produced by electrospinning of hydrophobic poly(ϵ -caprolactone) (PCL). Antifibrotic drugs (model ROCK inhibitors) can

be included in the spinning solution to afford drug-loaded fibers. Brief immersion of the PCL scaffolds in an alkaline solution led to the introduction of surface carboxylates, through which tetrazine group was immobilized via an amide bond. Separately, tetrazine or TCO- modified hyaluronic acid (HA-Tz and HA-TCO), as well as TCO-tagged cell adhesive peptide (RGD-TCO), were synthesized and characterized. Dipping tetrazine-functionalized PCL scaffolds in HA-TCO and HA-Tz baths in an alternating fashion resulted in the rapid build-up of a thick HA coating (1.7-2.0 mm) around individual fibers. Inclusion of RGD-TCO in the last HA-TCO bath led to the instantaneous conjugation of integrin-binding motifs to the fiber. Primary porcine vocal fold fibroblasts (PVFFs) were introduced to the drug-releasing core-shell scaffold and the culture was maintained for up to 14 days. Compared to the control PCL fibers, the core-shell fibers significantly suppressed the myofibroblast differentiation, as evidenced by positive α -smooth muscle actin (SMA) staining and the presence of mature stress fibers. Our results suggest that priming scar tissues with a fibrous patch that is soft and compliant, at the same time, releasing antifibrotic therapies in a controlled manner, will effectively suppress the fibrogenesis.

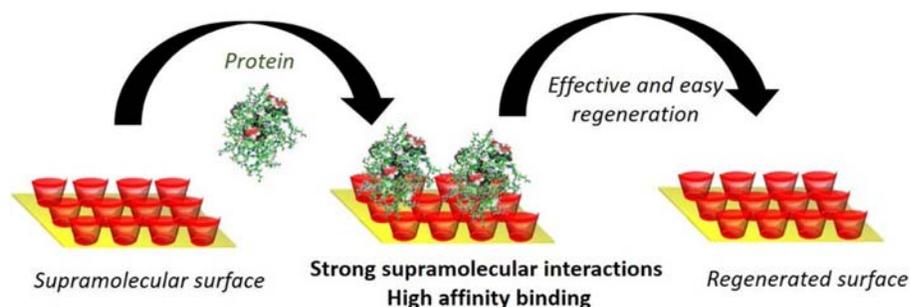
COLL 347

Supramolecular surfaces for protein immobilisation

Giuseppe Di Palma, giusdp45@gmail.com, Paula Mendes. School of Chemical Engineering, University of Birmingham, UK, Birmingham, United Kingdom

Protein immobilisation represents nowadays one of the most challenging fields in science and many technologies have been developed to meet a wide range of needs. Biosensors and biointerfaces, using the interaction of the protein with glucose, DNA or antibody are only a few examples of the huge amount of applications related to the concept of protein immobilisation. In spite of many signs of progress in the field, the best method to immobilise proteins on surfaces is still not well defined. The surface immobilisation of proteins is currently obtained mostly through covalent immobilisation or physical adsorption. Both methods, even considering the huge amount of applications they can have, still present some disadvantages. The supramolecular chemistry has the potential to overcome all these problems in a very elegant, fast and simple way by employing the host-guest interaction between a scaffold molecule and a protein. In this work, the host-guest interaction is enabled by a single step bottom-up nanofabrication of single-type self-assembled monolayers comprising cyclodextrin and cucurbituril moieties, which act as host molecules. On the other side, cytochrome C, insulin, α -chymotrypsin and RNase are used as representative guest proteins. The self-assembled monolayer of a single-type molecule was achieved with good surface packing as determined by contact angle, ellipsometry and cyclic voltammetry. Surface Plasmon Resonance (SPR) studies were conducted and supramolecular surfaces are shown to provide high affinity binding to the representative guest proteins. These results are supported by computational studies where, by the interaction understanding of a single amino-acid with the cyclodextrin moieties, it was possible also to predict the potential protein interaction points with the supramolecular surface. Furthermore, the

SPR results also show the possibility to reuse the surface multiple times by releasing the protein previously immobilised on it.



COLL 348

Metal – modified hydroxyapatites and their affinities for ions and molecules in solution

Spiro Alexandratos, alexsd@hunter.cuny.edu, Aiysha Ashfaq, Hila Benhaim, Marnie Kotlyar, Rubaya Yeahia. Hunter College City University of NY, New York, New York, United States

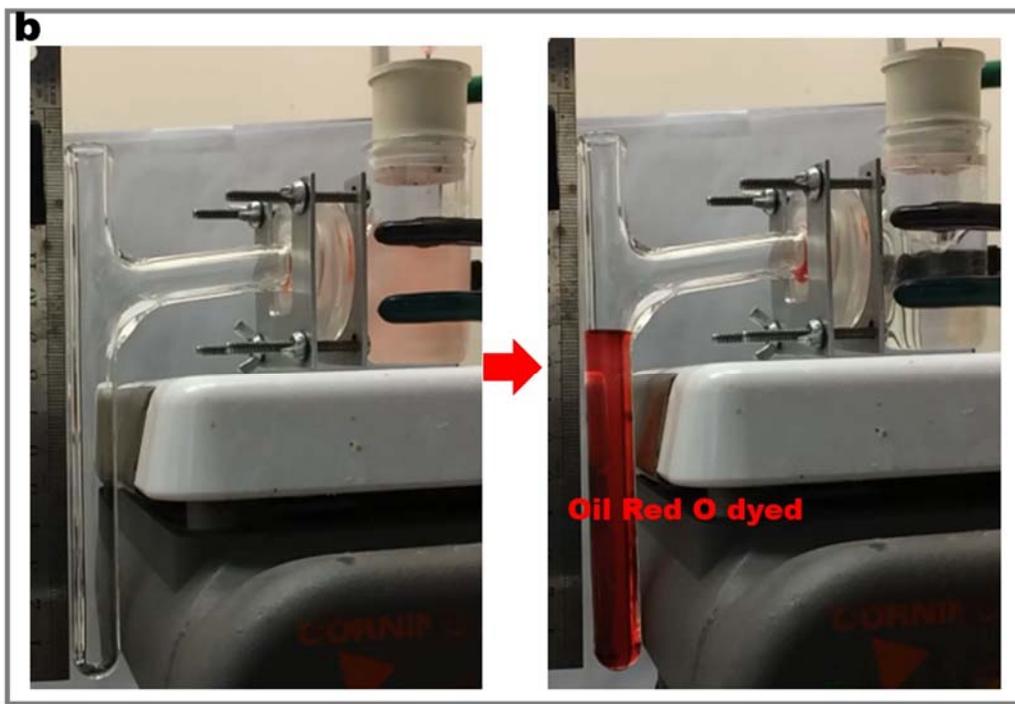
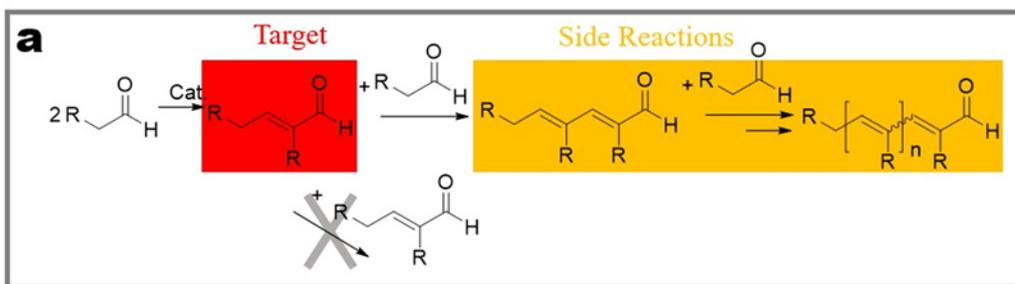
Hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is an important inorganic polymer that has been developed for bone tissue engineering due to its biocompatibility but which is also used as an adsorbent for metal ions and dyes in water. This presentation will focus on its use as an adsorbent and summarize progress in HAPs that have had a portion of their calcium ions substituted with other metal ions. Our latest results with metal – modified HAPs will be described.

COLL 349

Design of batch, semi-batch, and continuous reactor through superhydrophobic filter

Heng Hu¹, huheng_516@hotmail.com, Morgan Lehtinen³, Guojun Liu². (1) Chemistry, Queen's University, Kingston, Ontario, Canada (2) Dept Chemistry, Queens Univ, Kingston, Ontario, Canada (3) Chemistry, Queen's University, Kingston, Ontario, Canada

A lot of important organic synthesis have side reactions, and aldol condensation is one of the examples. Under the catalysis, the formed target product could under go further reactions with the raw material to yield annoying side-products (Scheme a). The further purification process costs extra labor and energy. Reported herein is a reactor with a superhydrophobic filter which could spontaneously separate the target product (oil) from the aqueous reaction medium (solvent, catalyst and reactant) in the first place by gravity force. Batch, semi-batch or continuous reactions were tested on this reactor, giving yield ~98%, and selectivity ~99% in the crude product (Scheme b).



Scheme a) Reaction leading to target and side-products. b) Reactor separated the product from the aqueous reaction medium.

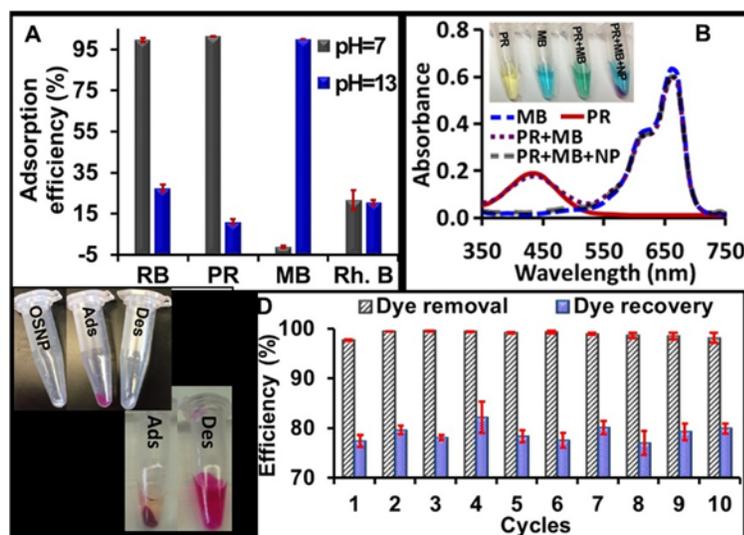
COLL 350

Tunable and repeatable dye adsorption/desorption via organosilica nanoparticles with an intrinsic amine

Fang Chen¹, fangch86@gmail.com, **Eric Zhao**¹, **Jesse V. Jokerst**². (1) NanoEngineering, UCSD, La Jolla, California, United States (2) NanoEngineering, UC San Diego, San Diego, California, United States

The adsorption/desorption ability of molecules onto substrates is important in drug delivery, nucleic acid isolation, water remediation, oil purification, and many other areas. Here, we synthesized an organosilica nanoparticle (OSNP) and studied its adsorption and desorption ability. The adsorption mechanisms are electrostatic attraction and

hydrogen bonding between the amine on OSNP and the dye. The OSNPs adsorb anionic molecules at pH 7 and cationic molecules at pH 13 (**Figure 1A**). The OSNPs adsorb only anionic dyes (>95%) from a mixture of anionic and cationic dyes at both ratios 1:10 and 1:1 when the pH is 7 (**Figure 1B**). Using phenol red as a model dye, we studied the effect of the amine group, pH, ionic strength, time, dye concentration, and nanomaterial mass on the adsorption. The theoretical and experimental maximum adsorption capacity are 175.44 mg/g and 201 mg/g, higher than 67 out of 77 reported adsorbents in the literature. Furthermore, the OSNPs are very reusable (**Figure 1C**) and show stable dye removal and recovery efficiency over at least 10 cycles (**Figure 1D**). In summary, the novel adsorbent system derived from the intrinsic amine group within the OSNP framework are reusable and tunable for anionic or cationic dyes with high adsorption capacity and fast adsorption. These materials may also have utility in drug delivery or as a carrier for imaging agents.



COLL 351

Effect of crystallite-size on the physical and chemical properties of nano-oxides

Siu-Wai Chan, sc174@columbia.edu. Applied Physics, Columbia University, NY, New York, United States

We will give an overview of the size-dependence lattice-parameter of nano-oxides where a lattice expansion of 0.1 to 0.5% as size decreases to ~5nm for five oxides suggesting a negative surface stress in each case. The five oxides are CeO₂, MgO, Cu₂O, Fe₃O₄, and Co₃O₄. The finding is different from the positive surface stress observed in nanoparticles of noble metals notably gold. Surface stress is calculated from the amount of lattice-contraction as crystallite-size decreases. The present investigation is possible because of the mono-dispersed nature of the nano-oxide in each batch. We have also studied the pressure and thermal response of the lattice-parameter of nano-ceria and nano-MgO.

Hence, bulk modulus (B) and coefficient of lattice thermal expansion (alpha) were

measured. Bulk modulus peaks around 33nm for nano-ceria and 14nm for nano-MgO. In both cases there is a quick decline below the peak. The findings have a number of implications for the bonding, surface-stress and elastic energy stored in these nanoparticles. Effects of surface adsorbents will be addressed with the help of earlier STM work on Fe₃O₄ (111) at Columbia University.

With binary oxides, the solubility of zirconia in nano-ceria is observed to be greater as the crystallite-size decreases and as the partial pressure of oxygen decreases. In reducing atmosphere, total solid solution in cubic fluorite structure is formed for full composition range of binary oxide of cerium and zirconium. Thus, the “bulk” phase diagram cannot predict the phases one might observe in nano-oxides. Even pure oxide of zirconium can be prepared in cubic fluorite structure with the right condition. Implication to their adsorption and catalytic properties will be discussed. Cation valence change, and defect density will be discussed when time allows.

COLL 352

Encapsulation of nanoscale hybrid materials for innovative CO₂ capture

Wei Yu², Ming Gao², Ah-Hyung A. Park¹, ap2622@columbia.edu. (1) Earth and Environmental Engineering & Chemical Engineering, Columbia University, New York, New York, United States (2) Earth and Environmental Engineering, Columbia University, New York, New York, United States

Fossil fuels, which significantly contribute to anthropogenic CO₂ emissions, are likely to remain the main source of energy in the foreseeable future. Therefore, the development of efficient carbon capture and storage (CCS) technologies is one of the great challenges faced by humanity. A new advancement in the area of CCS includes the development of the third-generation CO₂ capture materials. While a wide range of materials have been developed to capture CO₂ from flue gas ranging from aqueous amine solvents to solid sorbents, they are often challenged by high parasitic energy consumption during the solvent regeneration step. Thus, a new class of water-lean or anhydrous carbon capture materials such as Ionic Liquids (ILs) and Nanoparticle Organic Hybrid Materials (NOHMs) have been developed. One of the main challenges associated with their development is high viscosity. Thus, a new solvent delivery method via encapsulation has been proposed to provide large interfacial area for CO₂ capture for these viscous fluids. This study showed that NOHMs and other nanoscale materials can be successfully encapsulated inside UV-curing polymeric shell which is gas permeable. The CO₂ capture rate of the encapsulated solvents were drastically improved compared to bulk fluid. By tuning the fluid flow rates during encapsulation, the thickness of the shell can be controlled and, in some cases, multi core capsules were produced further increasing the interfacial area. This encapsulation technique can be applied to other systems with high viscosity.

COLL 353

Nanocomposite foam involving boron nitride nanoplatelets and polycaprolactone: Porous structures for oil spill cleanup

Lvhong Zhang, zhanglvhong@tju.edu.cn, Xiaowei Tantai. Tianjin University, Tianjin, China

Effective oil/water separation and removal of organic pollutants from water by taking advantage of new materials and techniques is essential for the protection of water sources and bodies throughout the world. Recently, polymeric nanocomposite materials have been the focus of intense research owing to high surface-to-volume ratio, enhanced absorption of nonpolar molecules promoted by increased attractive van der Waals interactions relative to polymers, and possibility to manipulate and tailor the internal nanostructure of polymeric base matrix to achieve high porosity and surface area.

We report a facile approach to fabricate highly porous nanocomposites made from polycaprolactone (PCL) and boron nitride (BN) nanoplatelets using high-energy intensity sonication-assisted coprecipitation mixing and supercritical CO₂ drying, which eliminates fractures and interfacial defects of such materials due to the excellent dispersion and distribution of the nanoparticles in polymeric hosts. The incorporation of BN nanoplatelets had two key benefits on PCL foam: First, the presence of BNNP enhanced the porosity and internal roughness of PCL foam. Second, BNNP also improved oil compatibility due to its nonpolar nature. Through a synergistic combination of surface morphology and interfacial tension effect, PCL:BNNP foams achieved a high hydrophobicity with a contact angle of 135° while being strongly oleophilic with a near zero contact angle for oils and nonpolar organic solvents. The absorption capacity was 6.1, 5.8, 4.3, 3.7, and 3.4 for paraffin oil, silicone oil, corn oil, hexadecane, and n-hexane, respectively. Additionally, the developed nanocomposite foam also exhibited low-density, mechanically stable, promising reusability and oil stability. Overall, this study offers a novel and facile strategy for fabricating porous nanocomposite materials with a strong potential in the applications of environmental remediation.

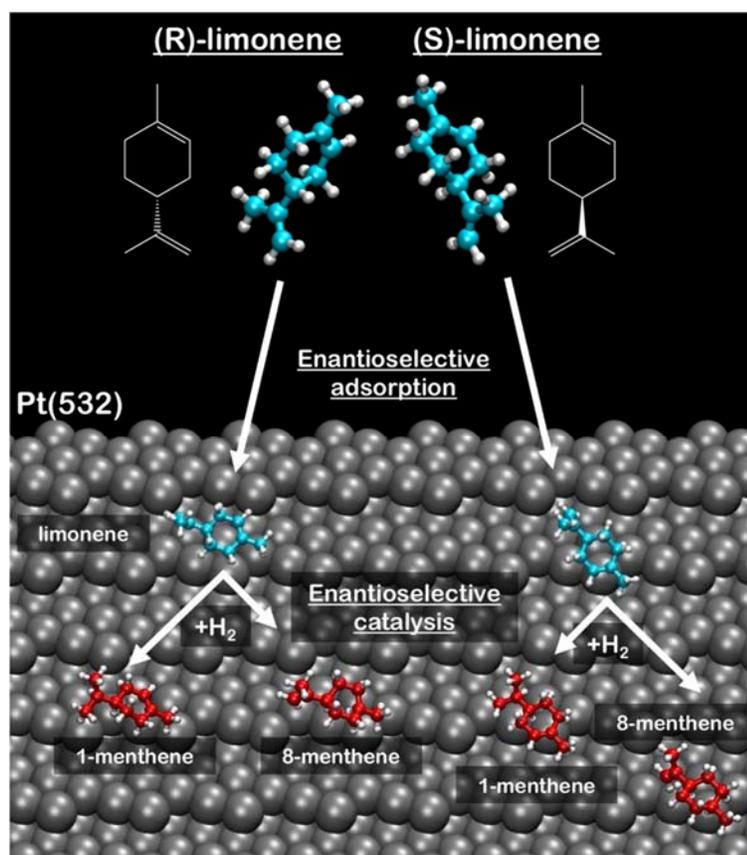
COLL 354

Chiral selectivity in heterogeneous catalysis

Robert C. Chapleski, rchaples@utk.edu, Sharani Roy. Chemistry, University of Tennessee, Knoxville, Knoxville, Tennessee, United States

Developing powerful next-generation technologies for catalysis, energy conversion, and energy storage relies on understanding and controlling molecular transformations at complex interfaces. However, relatively little is known about the fundamental molecular-scale phenomena driving chemical selectivity at functional and complex interfaces. Our work aims to investigate mechanisms of enantioselectivity in heterogeneous catalysis. Specifically, by investigating hydrogenation reactions of both the (R)- and (S)-

enantiomers of limonene on the chiral Pt(532) surface, we will provide insight into the adsorbate-surface interactions that lead to enantiomeric excess in the formation of the chiral product, menthene. Here, we report our initial results of this work, which uses computational methods to probe molecular adsorption of limonene followed by catalytic hydrogenation. Our approach utilizing density functional theory and molecular dynamics combined with the results of recent experimental sum-frequency generation experiments, reveals likely adsorption orientations and reaction pathways of both enantiomers on the Pt(532) surface. A comparison of adsorption and reaction mechanisms across both enantiomers leads to a fundamental description of the atomic-scale interactions that produce enantioselectivity in adsorption and reactions of limonene on a chiral platinum surface. We hope that these results provide qualitative insight into how enantioselectivity is achieved in heterogeneous catalysis at intrinsically chiral metal surfaces.



The (R)- and (S)- enantiomers of limonene adsorb differently onto the chiral Pt(532) surface. This enantioselective adsorption may be an initiating factor leading to differences in product formation resulting from limonene catalysis on Pt(532). Color scheme: C: blue/red, H: white, Pt: gray.

COLL 355

Nanoparticle electrocatalysts for chemical valorization of carbon dioxide

Peidong Yang^{1,3}, p_yang@berkeley.edu, Dohyung Kim^{2,3}. (1) Department of Chemistry, University of California, Berkeley, Berkeley, California, United States (2) Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States (3) Chemical Sciences Division, Lawrence Berkeley National Lab, Berkeley, California, United States

Finding innovative carbon management solutions is critical to ushering in a new era of sustainability. As a part of the many efforts in developing sustainable practices, electrochemical conversion of carbon dioxide to value-added products has gained significant interest due to its great potentials for fundamentally changing the way energy and matter flow in our society. In particular, research focused on nanomaterials based catalysts has provided significant breakthroughs in the field. Here, I will discuss the various structural aspects of nanoparticles used in electrocatalysis and how that understanding has led to improvements in their CO₂ reduction performance. The systematic approach to nanoparticle catalyst design requires the consideration of a wide range of length scales for their usage, from atomic all the way to macroscopic. First, we have explored the structural diversity of the gold-copper bimetallic nanoparticle system and probed the structural features down to atomic levels to evaluate their impact toward CO₂ catalysis. Then, we have sought ways to translate the identified active site motifs to more applicable platforms used in (photo-)electrochemistry. More recently, we have investigated the catalytic role of structural dynamics in nanomaterials electrochemistry, where the dynamic structural transformation of nanoparticles has been found to promote their CO₂ reduction activity. All the works discussed here will illustrate the large complexity of the structural variables involved in nanoparticle electrocatalysis and how the deepened understanding of that could benefit the catalytic transformations of CO₂ to valuable products.

COLL 356

Tuning catalytic activity in bimetallic transition metal phosphides via composition control

*Samuel I. Mutinda, Don M. Liyanage, Da Li, **Stephanie L. Brock**, sbrock@chem.wayne.edu. Chemistry, Wayne State University, Detroit, Michigan, United States*

Transition metal phosphides are proving to be versatile catalysts for a variety of reactions, including hydroprocessing of fossil and bio-fuels, and water-splitting. While initial studies focused on binary phosphide phases, dramatic performance improvements have been observed when ternary (bimetallic) phosphides are employed. In this presentation, we report on how compositional modulation in base-metal + noble metal bimetallic phosphides enables performance tuning for reduction vs. oxidation

processes, focusing on $M_{2-x}M'_xP$ ($M = \text{Co, Ni}; M' = \text{Ru, Rh}$). Synthetic considerations for achieving homogeneity in mixed metal systems involving first and second row transition metals, and the catalytic activity/stability of resultant materials towards complete water-splitting, will be discussed in the context of structure, site occupancy, electronic modulation and corrosion processes.

COLL 357

Interfacial engineering in two-dimensional nanomaterials for electrochemical/photoelectrochemical water splitting

Xinliang Feng, xinliang.feng@tu-dresden.de. Center for Advancing Electronics Dresden (cfaed), TU Dresden, Dresden, Saxon State, Germany

In this lecture, we will present our recent efforts on the design and synthesis of 2D nanomaterials-based electrocatalysts for the HER and OER, especially interfacial engineering of $\text{MoS}_2/\text{Ni}_3\text{S}_2$, NiFe-LDH/CoSe and $\text{Ni}_3\text{Se}_2/\text{Co}_9\text{S}_8$ heterostructures, tailoring water dissociation active sites of MoS_2 nanosheets, MoNi_4 , and NiFe-LDH nanosheets, as well as fabrication of 2D hierarchical MoS_2 nanosheets and porous cobalt phosphoselenide nanosheets. We will highlight their great potentials for enhancing the electrocatalytic water splitting performance. Moreover, we aim to address the fundamental correlations of kinetic reaction steps, electronic properties of active sites and water splitting activity.

COLL 358

Designing nanoparticle/electrolyte interfaces for dye-sensitized solar fuels

Yiyang Wu, wu@chemistry.ohio-state.edu. Ohio State Univ, Columbus, Ohio, United States

Tandem dye-sensitized photoelectrochemical cells (DSPECs) for water splitting are a promising method for sustainable energy conversion but so far have been limited by their lack of aqueous stability and photocurrent mismatch between the cathode and anode. In nature, membrane-enabled subcellular compartmentation is a general approach to control local chemical environments in the cell. The hydrophobic tails of the lipid make the bilayer impermeable to ions and hydrophilic molecules. Herein we report the use of an organic donor-acceptor dye that prevents both dye desorption and semiconductor degradation by mimicking the hydrophobic/hydrophilic properties of lipid bilayer membranes. The dual-functional photosensitizer (denoted as BH4) allows for efficient light harvesting while also protecting the semiconductor surface from protons and water via its hydrophobic π -linker. The protection afforded by this membrane-mimicking dye gives this system excellent stability in extremely acidic ($\text{pH} = 0$) conditions. The acidic stability also allows for the use of cubane molybdenum-sulfide cluster as the hydrogen evolution reaction (HER) catalyst. This system produces a proton-reducing current of $183 \pm 36 \mu\text{A}/\text{cm}^2$ (0 V vs NHE with 300 W Xe lamp) for an

unprecedented 16 hours with no degradation. These results introduce a method for developing high-current, low-pH DSPECs and are a significant move toward practical dye-sensitized solar fuel production.

COLL 359

Sequential partial cation exchange reactions as a pathway to complex heterostructured nanoparticle libraries

*Julie L. Fenton, Benjamin Steimle, **Raymond E. Schaak**,
schaak@chem.psu.edu. Pennsylvania State University, University Park, Pennsylvania,
United States*

Cation exchange reactions permit postsynthetic modification of metal chalcogenide nanoparticles. Arresting such reactions prior to completion leads to partial exchange and the formation of interfaces and multiple phases within the nanoparticles. We use the principles of nanoparticle cation exchange to define a modular divergent synthesis strategy that sequentially transforms copper sulfide nanoparticles into a library of complex heterostructured derivatives. Starting with first-generation (G1) copper sulfide spheres, rods, and hexagonal plates, we partially exchange the Cu^+ for Cd^{2+} or Zn^{2+} to define diverse intraparticle frameworks within second-generation (G2) nanoparticles. We then exchange the remaining Cu^+ to produce third-generation (G3) nanoparticles that retain the morphology of the G1 precursors and the intraparticle frameworks of the G2 intermediates, but have entirely different compositions. Subsequent reactions provide access to even more sophisticated heterostructured particles, including asymmetric, patchy, porous, and sculpted nanostructures.

COLL 360

Cesium lead halide perovskite nanocrystals for designing tandem architectures

*Vikas Ravi², Rebecca Scheidt², **Prashant V. Kamat**¹, pkamat@nd.edu. (1) University of Notre Dame, Notre Dame, Indiana, United States (2) Department of Chemistry, University of Notre Dame, South Bend, Indiana, United States*

Metal halide perovskite nanocrystals have received considerable attention in recent years because of the ability to tune their bandgap through halide ion composition. For example, by tailoring the ratio of Cl:Br and Br:I it is possible to modulate the absorption and emission properties of metal halide perovskites across the entire visible region. Relatively high emission quantum yield and long lived charge carriers make them suitable for photocatalytic reactions. Their sensitivity to chemical surroundings which induce chemical and morphological transformations pose a challenge for photocatalytic applications. The recently developed approach to cap nanocrystals with PbSO_4 -Oleate offers an interesting strategy to overcome some stability issues. The results that highlight photodynamics and charge separation in CsPbBr_3 and CsPbI_3 nanocrystals (with and without PbSO_4 -Oleate capping) will be presented. The design of tandem

structures using mixed halides for photocatalytic and photovoltaic application will be discussed.

COLL 361

Nanocatalysts for green fuel production

Hua-Chun Zeng, *chezhc@nus.edu.sg. Chem Biomol Eng, Natl Univ Singapore, Singapore, Singapore*

Our research is focused on design and synthesis of integrated nanocatalysts for green fuel technology such as hydrogenation of CO₂ to methanol. In preparing such new catalysts, various synthetic approaches have been developed in recent years. Normally, the primary catalytic phases are synthesized into monodisperse nanoparticles through wet chemical routes, while the hosting matrixes are often prepared as porous and/or hollow supports in solution with desired structural complexity and chemical functionality. In particular, integration of different catalytic components can be achieved in a step-by-step manner. Both *top-down* and *bottom-up* strategies have been employed in this type of synthetic architecture, benefiting from rapid advancement of nanoscience and nanotechnology as well as the maturing chemistry of materials. It is anticipated that structural and compositional requirements of such state-of-the-art nanocatalysts can be met at a higher level of sophistication and precision but at a much lower cost in future. Toward this goal, synthetic architecture of nanomaterials will continue to be an important field in future development of catalyst technology. Further investigation and invention of integrative methodology will lead to even more powerful catalysts, achieving an industrial scale of applications.

COLL 362

Thermoplasmonics: Fundamentals and application to targeted hyperthermia

Romain Quidant, *romain.quidant@icfo.es. ICFO, Barcelona, Spain*

For a long time, the absorption of resonant metal nanoparticles (MNPs) and their subsequent temperature increase have been considered as side effects in the field plasmonics. Only recently have scientists realized that this enhanced light absorption, turning MNPs into ideal nano-sources of heat remotely controllable by light, provides an unprecedented way to control thermal-induced phenomena in a wide range of application including information technology, chemistry and medicine.

The first purpose of this talk is to describe the unique photothermal properties of MNPs and how they can enable us to control heat generation on a nanometer scale under ultra-fast dynamics. In this context, we also present the tool box we have developed to predict and experimentally characterized these properties.

Next, we identify the optimum geometries for targeted hyperthermia in vivo. This is

based on a systematic study of the most critical parameters involved in light-to-heat conversion, accounting for both cell toxicity and uptake.

Finally, we present our latest advances in the actual implementation of light-induced targeted hyperthermia in vivo, to different biomedical contexts.

COLL 363

Photothermal-driven drug-delivery nanoplatform based on plasmonic zeolitic imidazolate frameworks

Carolina Carrillo Carrion, *carolcc83@hotmail.com*, Pablo del Pino. BioNanoTools Lab, CiQUS, University Santiago de Compostela, Santiago de Compostela, Spain

In recent years, the interest in nanoscale materials for theranostic applications, for instance against cancer, has increased. In this direction, multifunctional hybrid nanostructures with improved bioperformance in real scenarios are required. The combination of plasmonic nanoparticles such as gold nanoparticles with metal-organic frameworks (MOFs) offers unique opportunities for the development of nanoplatforms with theranostic potential thanks to the versatile drug encapsulation properties of metal-organic frameworks, such as well-defined pore aperture, tunable pore size, and tailorable composition and structure. Here, we present a hybrid nanostructure based on zeolitic imidazolate framework-8 growth around pre-stabilized gold nanorods (ZIF-8@AuNR). Surface functionalization of the composites is required to make them stable in aqueous medium as well as cell culture medium for bioapplications. Complementary techniques such as UV-Vis spectroscopy, X-ray diffraction and dynamic laser-light scattering (DLS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are performed in order to characterize the physicochemical properties of the composites and the colloidal stability under different conditions. Moreover, to evaluate their potential as a drug delivery nanoplatform, the encapsulation of several drugs and the subsequent photothermal-driven release have been investigated.

COLL 364

Luminescent nanoparticles to optically monitor plasmonic heating within the biological windows

Marta Quintanilla¹, *mquintanilla@cicbiomagune.es*, Isabel García², Irene de Lázaro del Rey³, Sandra Vranic³, Ana Sánchez-Iglesias¹, Kostas Kostarelos³, Luis Liz Marzan⁴. (1) CIC BiomaGUNE, San Sebastian, Gipuzkoa, Spain (2) CIC BiomaGUNE, San Sebastian, Spain (3) Faculty of Biology, Medical & Health, University of Manchester, Manchester, United Kingdom (4) CIC biomaGUNE, Donostia - San Sebastian, Spain

In biomedical applications that rely on light triggering an effect, the heterogeneity of biological tissues complicates the prediction of the intensity of light reaching each inner

spot. As a consequence, for the specific case of photothermal therapy in which a thermal increase is created by nanoparticles that absorb light and release heat, the achieved temperature is only approximately known. Typically, to kill infected cells through photothermal treatments a temperature between 40 and 60 °C is required, depending the exact value on the duration of the treatment. If the reached temperature is too low, the therapeutic effect wouldn't be enough, if too high, extended damage beyond the size of the infected area may happen. In order to gain control on the actual temperature applied during a photothermal treatment, it is possible to use luminescent nanoparticles whose light emission depends on temperature. A particularly suitable option is to exploit the luminescence of neodymium-doped CaF₂ nanoparticles, as both their excitation and emission wavelengths lay within the regions in which biological tissues present a lower extinction coefficient, i.e. within the biological windows. However, accurate thermal reading requires optimization both of the material and the measuring strategy. Combining these thermometric nanoparticles with gold nanoparticles with the plasmon resonance within the biological windows, a heating platform that can be monitored *in situ* is created.

COLL 365

Nanomaterials for cell tracking applications - How to enhance the contrast

Neus Feliu, nfeliu@physnet.uni-hamburg.de, Wolfgang Parak. Universitaet Hamburg, Hamburg, Germany

Nanomaterials offer promising opportunities for a wide range of applications including medicine. Their novel properties make them excellent imaging and diagnostic agents. However, nanoparticles could be potentially harmful for humans and environment. To understand the possible effects of nanoparticles exposed to biological systems, a detail association of such effects to the physicochemical properties of the nanoparticles is needed. Therefore, we will provide an overview of the common denominators to evaluate the nanosafety research, and discuss the potential use of an advanced system based on nanoparticle-based imaging labels to monitor stem cells non-invasively *in vivo*. A deeper understanding in these areas will help to improve the development of nanomaterials for medical applications. In particular it will be discussed how the maximum amount of nanoparticles can be applied to cells as label, without harming cells.

COLL 366

Stem cells transporting gold nanorods

Jacob M. Berlin, jberlin@coh.org. Molecular Medicine, Beckman Research Institute at City of Hope, Duarte, California, United States

Plasmonic photothermal therapy utilizes biologically inert gold nanorods (AuNRs) as tumor-localized antennas that convert light into heat capable of eliminating cancerous

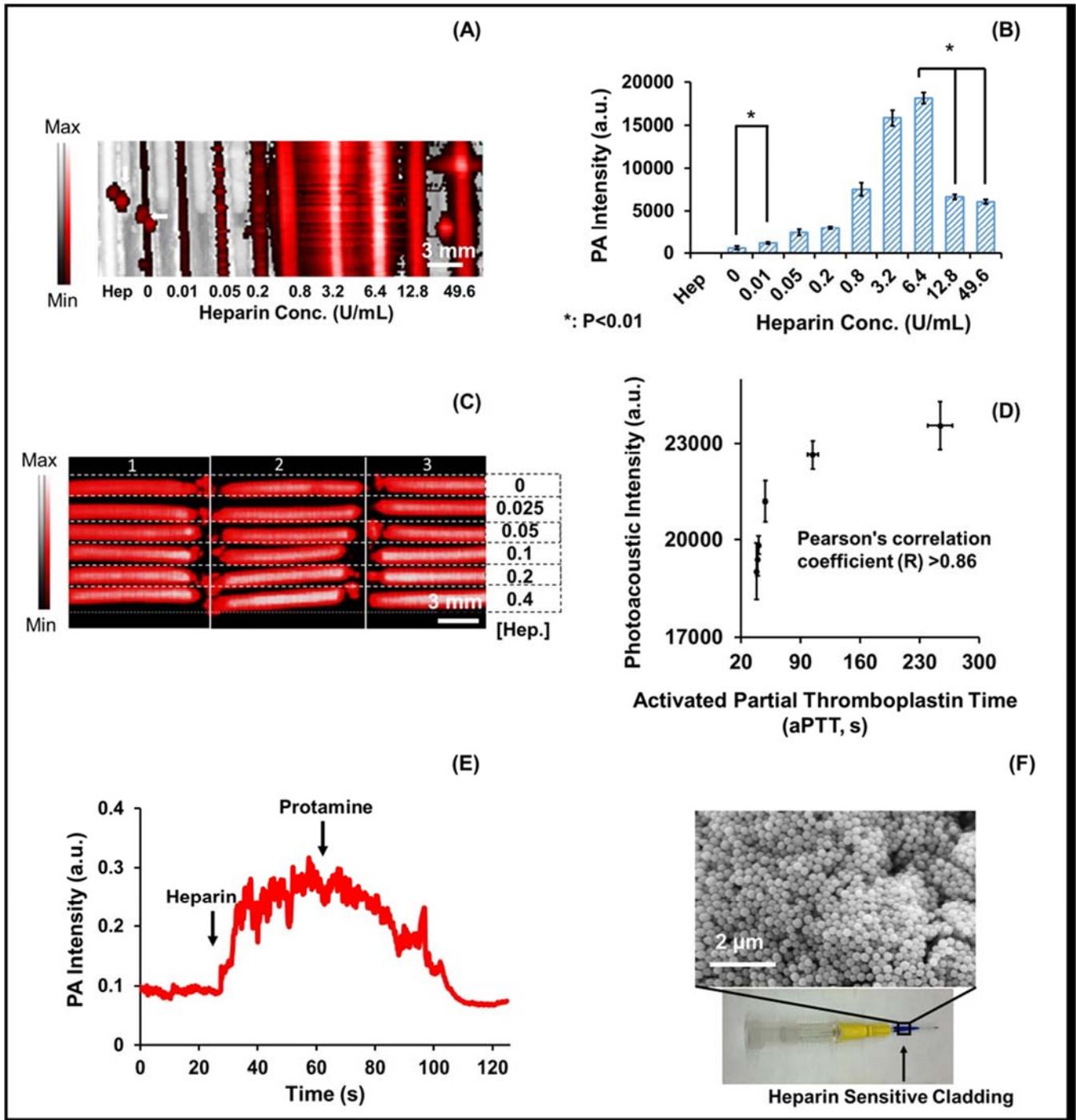
tissue. This approach has lower morbidity than surgical resection and can potentially synergize with other treatment modalities including chemotherapy and immunotherapy. Despite these advantages, it is still challenging to obtain heating of the entire tumor mass while avoiding unnecessary collateral damage to surrounding healthy tissue. It is therefore critical to identify innovative methods to distribute an effective concentration of AuNRs throughout tumors without depositing them in surrounding healthy tissue. Here we demonstrate that AuNR-loaded, tumor-tropic neural stem cells (NSCs) can be used to improve the intratumoral distribution of AuNRs. A simple UV-Vis technique for measuring AuNR loading within NSCs was established. It was then confirmed that NSC viability is unimpaired following AuNR-loading and that NSCs retain AuNRs long enough to migrate throughout tumors. We then demonstrate that intratumoral injections of AuNR-loaded NSCs are more efficacious than free AuNR injections as evidenced by reduced recurrence rates of triple negative breast cancer (MDA-MB-231) xenografts following NIR exposure. Finally, we demonstrate that the distribution of AuNRs throughout the tumors is improved when transported by NSCs, likely resulting in the improved efficacy of AuNR-loaded NSCs as compared to free AuNRs. These findings highlight the advantage of combining cellular therapies and nanotechnology to generate more effective cancer treatments.

COLL 367

Heparin and clotting time measurements via photoacoustic imaging and a silica-nanoparticle/hydrogel hybrid

Junxin Wang, junxinud@gmail.com, Fang Chen, Santiago Arconada, Jesse V. Jokerst. University of California San Diego, La Jolla, California, United States

Heparin is an indispensable anticoagulant yet remains difficult to control because of its small therapeutic window. The active partial thromboplastin time (aPTT) is the gold standard clotting time measurement method in laboratory; however, it is unable to provide a stable, accurate, and real-time feedback of heparin and dose, which are vital to patients poisoned by heparin. Here, we used a Federal Drug Administration-approved contrast agent methylene blue (MB) to measure heparin via real-time photoacoustic imaging. The photoacoustic signal of MB is significantly increased upon addition of heparin (**Panel A**) and strongly correlated to the heparin concentration in phosphate buffered saline (PBS) ($R^2 > 0.98$) (**Panel B**) and blood ($R^2 > 0.97$) (**Panel C**). Additionally, the photoacoustic intensity in blood is well correlated with the aPTT (Pearson's $r = 0.86$; $p < 0.05$) (**Panel D**). We also detected 3 U/mL (i.e. a clinically relevant heparin concentration) in blood in 32 s and the signal is reversible with protamine sulfate treatment (**Panel E**). This technique can also measure concentrations of an important alternative of heparin low molecular weight heparin (enoxaparin) as low as 72 $\mu\text{g/mL}$ in blood. Finally, we hybridized agarose with silica nanoparticles loaded with MB as a coating material on catheters for implantable heparin measurements (**Panel F**). The surface charge of silica nanoparticle was optimized to increase the detection limit of heparin.



Panel A and B show the photoacoustic intensity and the corresponding statistics of MB with increasing concentrations of heparin. This photoacoustic response was also characterized in blood (panel C) and compared with aPTT (panel D). Panel E and F reveal the detection speed the hydrogel coated catheter.

COLL 368

N- and P-doping of colloidal nanocrystal and nanowire assemblies

Cherie R. Kagan, *kagan@seas.upenn.edu*. Dept of ESE MSE, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States

Doping is used to control free carrier type and concentration in semiconductor materials. In bulk semiconductors, doping is conventionally achieved through impurity substitution, and less well-known, by controlling a material's stoichiometry. However, doping in low-dimensional, colloidal semiconductors presents both new opportunities and challenges. The electron and hole concentrations in colloidal nanocrystal (NC) and nanowire (NW) assemblies have often been manipulated by "remote doping," exploiting the large surface-to-volume ratio of nanostructures to add atoms, ions, or ligands to the surface that serve as dopants. For example, we describe methods of 1) thermal evaporation and diffusion and 2) wet-chemical techniques to introduce extrinsic impurities to and non-stoichiometry through the nanostructure surface to passivate surface traps and dope NC and NW assemblies. However, the doping efficiency of colloidal nanostructures is often extremely low, such that only 1% of dopants yield carriers. These low doping efficiencies are consistent with increased ionization energies from quantum and dielectric confinement effects. We show for a given size nanostructure, where quantum confinement effects are fixed, the doping efficiency can be enhanced by >10-fold by encapsulating the NCs and NWs in high dielectric constant materials that reduce the dielectric mismatch between the nanostructure and its surroundings. We give examples where n- and p-type semiconductor NC and NW assemblies are used to construct flexible, electronic transistors and integrated circuits and optoelectronic solar photovoltaics and photodetectors.

COLL 369

To dope semiconductor nanocrystals: Chalcogenides to perovskites

Narayan Pradhan, *camnp@iacs.res.in*. Materials Science, Indian Association for the Cultivation of Science, Kolkata, India

Introducing few atoms of impurities or dopants in semiconductor nanocrystals can drastically alter the existing or even introduce new properties. For example, mid-gap states created by doping tremendously affect photocatalytic activities and surface controlled redox reactions, generate new emission centres, show thermometric optical switching, make suitable FRET donors by enhancing the excited state lifetime and also create localized surface plasmon resonance induced low energy absorption. These dopant-induced beneficial changes in material properties suggest that doped nanocrystals with proper selections of dopant-host pairs, may be helpful for generating designer materials for a wide range of current technological needs. While doping was mostly studied in chalcogenide nanocrystals, these were now also extended to perovskite nanocrystals. The talk would present the doping chemistry, dopant induced

change in optical emission and some novel approach of doping of different chalcogenides and perovskite nanocrystals.

COLL 370

Hybrid materials based on colloidal nanocrystals: From synthesis to emerging properties for energy storage in chemical bonds

Raffaella Buonsanti, raffaella.buonsanti@epfl.ch. EPFL, Sion, Switzerland

Energy devices require materials able to transport mass, charge and energy during operation. Such a complexity of functions is hard to meet by single component materials. Therefore, the demand for hybrid multifunctional materials has been increasing in different applications.

Our group is assembling colloidal nanocrystals with building blocks of different classes of materials, such as polymers, metal organic frameworks, fully inorganic oxide matrices. The goal here is to establish novel synthetic schemes to achieve an exquisite control and tunability of these hybrids across multiple length-scales by understanding and manipulating the nucleation and growth kinetics. Our current focus is to build material platforms to advance studies in the conversion of water and CO₂ into value added chemicals.

In this talk, I will focus on the role of ligands and surface chemistry in the synthesis of different hybrid architectures including copper nanocrystals. I will present some of our most recent solid-state NMR data and in-situ X-Ray diffraction studies. The latter allows to get insights into the kinetics behind chemical transformations at the nanoscale.

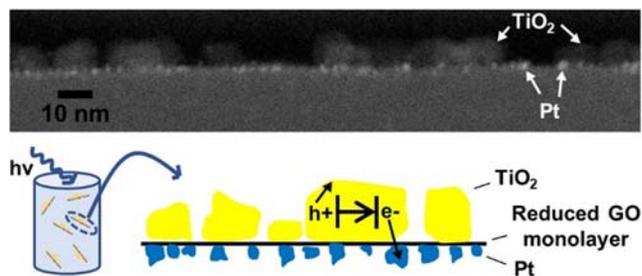
COLL 371

Synthesis, characterization and light-induced spatial charge separation in Janus graphene oxide

Alexander Holm¹, aholm@stanford.edu, Joonsuk Park², Emmett D. Goodman¹, Jiaming Zhang³, Robert Sinclair², Matteo Cargnello¹, Curtis W. Frank¹. (1) Chemical Engineering, Stanford University, Stanford, California, United States (2) Materials Science, Stanford University, Stanford, California, United States (3) Hewlett Packard, Palo Alto, California, United States

Janus graphene oxides and Janus graphenes have different functionalization on opposite surfaces of atomically thin sheets. These materials have recently emerged as a new class of two-dimensional Janus particles, and owing to their extremely thin nature, these Janus sheets provide ideal platforms for asymmetric chemistries. Here, we describe synthesis of Janus graphene oxide, asymmetrically functionalized with titania and platinum particles. We used a silicon wafer and a polymer film to successively expose and protect alternate graphene oxide (GO) faces for asymmetric deposition of Pt and TiO₂ nanocrystals, thus producing Janus graphene oxide particles (Pt|GO|TiO₂). We followed specific individual sheets throughout the whole asymmetric

functionalization process with atomic force microscopy and Raman microscopy. We used electron microscopy of Janus graphene oxide cross-sections to directly and conclusively show Pt and TiO₂ particles on opposite faces of monolayer GO sheets. Spatial separation of electrons and holes in Pt|GO|TiO₂, dispersed in solution, was demonstrated by photoinduced selective deposition of Pd onto Pt. The selective deposition suggests that in our Pt|GO|TiO₂ Janus graphene oxide, photogenerated electrons and holes accumulated on opposite faces of the atomically thin sheets. Janus graphene oxides could be synthesized with many material combinations and may therefore provide a general method for spatial separation of charges across two-dimensional structures in several systems.



COLL 372

From inside out: How buried interface, defects and surface determines performance of two giant core-shell quantum dots

Ajay Singh^{1,2}, ajaysingh@lbl.gov, Somak Majumder¹, Noah J. Orfield¹, Han Htoon¹, Jennifer A. Hollingsworth¹, Karen Bustillo², Jim Ciston². (1) Materials Physics and Applications Division-Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) NCEM- Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States

Colloidal quantum dots (CQDs) are attractive materials for lasers, displays and other light-emitting applications due to their size-tunable bandgap, narrowband photoluminescence, and potential for high quantum yields (QYs) in emission. However, in light and air CQDs undergo degradation of their optical properties over time due to photo-oxidative processes at their surfaces. To overcome this limitation, several approaches have been used, including overcoating with an inorganic semiconductor shell of a wider bandgap (core/shell heterostructures), surface functionalization with ligands or polymer coatings, and embedding in organic or inorganic matrices. In particular, we have developed a novel core/shell architecture involving an ultra-thick or “giant” shell, where the resulting giant CQDs (g-CQD) can afford complete suppression of blinking behavior (fluorescence intermittency) and absence of room-temperature photobleaching, in stark contrast with conventional core/shell CQD architectures. Despite significant recent progress in the development of a family of g-CQDs, spanning the visible and infrared spectral ranges, the precise nature of the core/shell interface, the shell properties, and the g-CQD surface properties lack sufficient elucidation. Here, we describe the first detailed characterization of these key aspects of the g-CQD

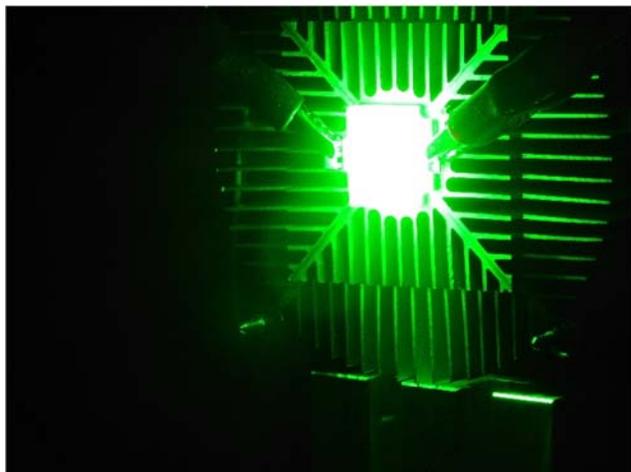
structure, including a quantitative assessment of interfacial alloying, shell defect density and surface composition. Our assessment takes advantage of both single-nanocrystal-level characterization (aberration-corrected electron microscopy, elemental mapping) and ensemble level characterization (powder x-ray diffraction, synchrotron-enabled x-ray photoelectron spectroscopy) to accurately describe the subtle differences between g-CQDs that lead to substantive differences in optical properties and long-term photostability. Lastly, we show that through correlated analyses, we can draw causative relationships between synthesis parameters, nanocrystal structure and g-CQD performance toward new and optimal materials design.

COLL 373

Aggregation-induced emission in lamellar solids of colloidal perovskite quantum wells

Chih-Jen Shih, *chih-jen.shih@chem.ethz.ch*. Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland

The outstanding excitonic properties, including photoluminescence quantum yield (η_{PL}), of individual, quantum-confined semiconductor nanoparticles are often significantly quenched upon aggregation, representing the main obstacle toward scalable photonic devices. We report aggregation-induced emission phenomena in lamellar solids containing layer-controlled colloidal quantum wells (QWs) of hybrid organic-inorganic lead bromide perovskites, resulting in anomalously high solid-state η_{PL} of up to 94%. Upon forming the QW solids, we observe an inverse correlation between exciton lifetime and η_{PL} , distinct from that in typical quantum dot solid systems. Our multiscale theoretical analysis reveals that, in a lamellar solid, the collective motion of the surface organic cations is more restricted to orient along the [100] direction, thereby inducing a more direct bandgap that facilitates radiative recombination. Using the QW solids, we demonstrate ultrapure green emission by completely downconverting a blue gallium nitride light-emitting diode at room temperature, with a luminous efficacy higher than 90 lumen W^{-1} at 5000 cd m^{-2} , which has never been reached in any nanomaterial assemblies by far.



Bright and ultrapure green electroluminescence generated by 100% downconverting a blue LED using the AIE quantum well solids.

COLL 374

Spectroscopic evidence of conduction band fine structure in colloidal HgTe quantum dots with well-defined intraband transitions

Margaret H. Hudson¹, mhhudson@uchicago.edu, Menglu Chen³, Philippe Guyot-Sionnest³, Dmitri Talapin^{1,2}. (1) Department of Chemistry, University of Chicago, Chicago, Illinois, United States (2) Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, United States (3) James Franck Institute, University of Chicago, Chicago, Illinois, United States

HgTe colloidal quantum dots (QDs) are of interest because quantum confinement of semimetallic bulk HgTe allows one to synthetically control the bandgap throughout the infrared. Here, we synthesize high quality HgTe QDs and tune the doping both chemically and electrochemically. Electron-doped HgTe QDs display an intraband absorbance and bleaching of the first two excitonic features. Unlike previous studies of doped QDs, we see splitting of the intraband peaks corresponding to electronic transitions from the doped $1S_e$ state to a series of non-degenerate $1P_e$ states. Spectroelectrochemical studies reveal that the degree of splitting and relative oscillator strength of the intraband absorbance features remain constant across doping levels up to two electrons per QD. Moreover, we find that in QDs of different sizes the energy and degree of splitting of the intraband peaks vary linearly with confinement energy. Theoretical modeling suggests that the splitting of the $1P_e$ level arises from a combination of spin-orbit coupling and structural asymmetry. We postulate that split intraband features are first observed here due to the size uniformity of the as-synthesized QDs and strong spin-orbit coupling inherent to HgTe. The monodispersity of the QDs was evaluated using absorption, SAXS, and self-assembly and suggests a diameter distribution of $\sim 10\%$ across multiple synthesized batches of different sizes.

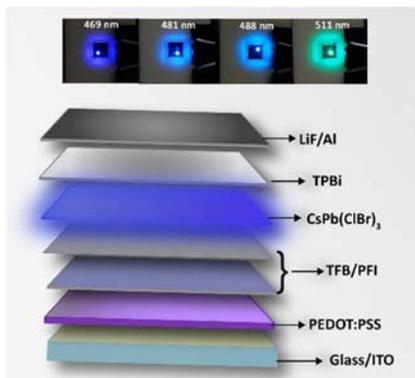
COLL 375

Blue perovskite nanocrystals for quantum dot light emitting diodes

Mahesh Gangishetty, gangishetty@rowland.harvard.edu, Shaocong Hou, Qimin Quan, Daniel Congreve. Rowland Institute, Harvard University, Cambridge, Massachusetts, United States

Colloidal nanocrystals of $CsPbX_3$ have found potential opportunities in quantum dot light emitting diodes (QLEDs) due to their highly tunable optical properties. Green and red nanocrystals are progressing rapidly in QLEDs with efficiencies over 5%. Blue nanocrystals, however, are still lagging far behind red and green owing to their poor PLQYs. The best efficiency reported on these blue perovskite QLEDs is only 0.07%.

Our group, recently discovered that in addition to the PLQYs, the transport layers play a crucial in the device performance. By employing a combination of HTL and a buffer layer (TFB:PFI), we achieved ~7 fold increase in the efficiency to 0.5%. Further, we improved the quality of nanocrystals by doping with Mn, which eventually lead to a factor of 4x enhancement in the EQE (2.1%) with a FWHM of 17 nm, meeting the standards of pure NTSC blue coordinates. We then used down converting green and red nanocrystals to construct all perovskite white LEDs for the first time. In this talk, I will discuss the evolution of blue nanocrystals in LEDs and the impact of Mn doping on their PLQY and device performance.



COLL 376

Controlled dopant migration in core/shell semiconductor nanocrystals

Weiwei Zheng, wzhen104@syr.edu. Chemistry, Syracuse University, Syracuse, New York, United States

The physical properties of a doped semiconductor nanocrystals (NCs) are strongly influenced by the dopant site inside the host lattice, which determines the host–dopant coupling from the overlap between the dopant and exciton wavefunctions of the host lattice. Although several synthetic methodologies have been developed for introducing dopants inside the size-confined semiconductor NCs, the controlled dopant–host lattice coupling by dopant migration is largely unexplored. In this work, the effect of lattice mismatch of core/shell NCs (including CdS/ZnS and ZnSe/ZnS core/shell NCs) on Mn(II) dopant behavior was studied. It was found that the dopant migration toward the alloyed interface of core/shell NCs is a thermodynamically driven process to minimize the lattice strain within the NCs. The dopant migration rate could be represented by the Arrhenius equation and therefore can be controlled by the temperature and lattice mismatch. Furthermore, the energy transfer between host NCs and dopants can be finely turned in a wide range by dopant migration toward the alloyed interface during ZnS shell passivation, which provides an efficient method to control both the number of the emission band and the ratio of the emission from the host lattice and dopant ions.

COLL 377

Initial surface chemistry of nanoparticles has cascading impacts on biological systems

Catherine J. Murphy, *murphycj@illinois.edu*. Box 59-6, Univ of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Colloidal nanoparticles, as made in the lab, display a variety of ligands, ions, and other surface groups to the aqueous environment. It is well-known that colloidal nanoparticles in the biological milieu will acquire molecular coronas, most famously proteins, and thereby cover up all the initial surface chemistry. Yet in experiment after experiment, the initial surface chemistry of the nanoparticle does indeed dictate biological outcomes – even if we cannot say for sure the exact mechanism. In this talk I will show data from my lab and others' that illustrates these points, and provide some speculation about mechanisms that should be rigorously examined.

COLL 378

Engineering unusual properties on the nanoscale: Smart nanomicelles for targeting tumor microenvironments

Shuming Nie¹, *nies@illinois.edu*, Jinzhi Du². (1) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) South China University of Technology, Guangzhou, Guangdong, China

The design and development of sophisticated nanoparticles for the targeted delivery of therapeutic drugs to solid tumors holds great promise not only for improving treatment efficacy but also for reducing systemic toxicity. However, the currently low delivery efficiency (about 1-5 % of the injected dose) and the limited tumor penetration of nanoparticles remain two major challenges. Here we report a class of nanoscale superstructures with unusual pH-responsive and size-switching properties for targeting the acidic tumor microenvironment as well as for improved drug tumor penetration. Specifically, the supernanostructures are constructed by using pegylated polymethacrylate copolymers containing tertiary amine groups (sensitive to pH), and the protonation or deprotonation of these tertiary amines induces a dramatic hydrophobic-hydrophilic transition which drives rapid assembly or disassembly on the nanoscale. These superstructures have a relatively large size of about 80 nm at neutral pH (blood circulation), but once deposited in the acidic tumor microenvironment (pH ~6.5-7.0), they undergo a dramatic and sharp size transition within a very narrow range of acidity (less than 0.1-0.2 pH units), and dissociate rapidly into building blocks (less than 10 nm in diameter). This rapid size-switching feature can not only facilitate nanoparticle extravasation and accumulation via the enhanced permeability and retention (EPR) effect, but also allows faster nanoparticle diffusion and improved tumor penetration. The results demonstrate that the high pH sensitivity and particle size switching are indeed viable strategies for improving drug penetration and therapeutic efficacy.

COLL 379

Gold nanoparticle radiosensitization – the road traveled, the road ahead

Sunil Krishnan, skrishnan@mdanderson.org. MD Anderson Cancer Center, Houston, Texas, United States

An evolving body of recent literature alludes to the potential to sensitize tumors to radiation therapy using metallic nanoparticles. In preclinical studies, a technique that holds promise for eventual clinical deployment is nanoparticle-assisted radiation dose enhancement. Computational techniques offer an explanation for and predict the biophysical consequences at a nano-/meso-scopic scale. Preclinical studies in vitro and in vivo provide evidence of radiosensitization. Nonetheless, there are persisting gaps in knowledge relating to the molecular mechanism of action and optimum nanoparticle characteristics – some of these issues will be addressed. My presentation will start with familiarizing the audience with the potential applications of gold nanoparticles in radiation therapy using specific illustrative examples, explore ways to understand the underlying mechanisms of the effects observed, and provide a perspective on how to advance these concepts to the clinic.

COLL 380

Porphysome nanotechnology: From discovery to translation

Gang Zheng^{1,2}, gang.zheng@uhnres.utoronto.ca. (1) Princess Margaret Cancer Centre, Toronto, Ontario, Canada (2) Department of Medical Biophysics, University of Toronto, Toronto, Ontario, Canada

Porphyrins are aromatic, organic, light-absorbing molecules that occur abundantly in nature, especially in the form of molecular self-assemblies. By conjugating porphyrins to lipids, we formed porphysomes, self-assembled liposome-like nanoparticles with intrinsic multimodal photonic properties. High-density porphyrin packing in the nanoparticle bilayer enables light absorption and conversion to heat with extremely high efficiency, making porphysomes ideal candidates for photothermal therapy and photoacoustic imaging. Upon nanostructure dissociation during cell uptake, the fluorescence and photodynamic activity of the porphyrin monomers is restored. In addition, metal ions can be directly incorporated into the porphyrin building blocks of the preformed porphysomes, thus unlocking their potential for PET and MRI. By changing the way porphyrin-lipids assemble, we developed HDL-like porphyrin nanoparticles (<20 nm), porphyrin microbubbles (~2 µm), giant porphyrin vesicles (~100 µm), hybrid porphyrin-gold nanoparticles, and metal-chelating nanotexaphyrins. We have validated porphysome's multimodal utilities in different cancer types, tumor models, and animal species. The effort of moving porphysomes towards first-in-human use is well on its way. In summary, the simple yet intrinsic multimodal nature of porphysomes represents a new nanomedicine paradigm and also confers high clinical translation potential.

COLL 381

Thermally triggered nano-assassins for pancreatic cancer therapy

Clare Hoskins, *c.hoskins@keele.ac.uk*. School of Pharmacy, Keele University, Keele, United Kingdom

Pancreatic cancer treatment has not progressed in the last few decades. Patient treatment options are severely limited and often mortality is the outcome. We are working towards providing strategies to overcome the four principle challenges identified in the development of pancreatic cancer therapies for late stage cancers. These are: Poor drug efficacy due to hindered penetration through dense stromal barriers; Systemic circulation of highly toxic chemotherapies; Premature release and lack of site specificity resulting in off target effects; *In vivo* fate / clearance of nanoparticles after administration.

To start to overcome these challenges, we development of multifunctional nanotechnologies with the capability for image guidance, targeting, deep penetration, and controllable drug release. Our group has developed hybrid iron oxide-gold nanoparticles (HNPs) as thermally activated drug delivery systems. The multicomponent nature of these nanoparticles renders them not only suitable as imaging agents *via* MRI but also the ability to act as heat sources after laser irradiation of the gold surface.

The fabrication, optimization, characterisation and physical properties of these systems has been determined. We have tested their biocompatibility and heating effect both in phantoms cells and cadavers. We have determined the effect of laser irradiation at our wavelength and at various HNP concentrations on the cellular state of pancreatic adenocarcinoma cells and any resultant heat shock protein production. Our proof recent studies trialled two different attachment and release strategies for conjugation onto the HNPs. Firstly, we explored the effectiveness of electrostatically conjugating charged drug molecules directly onto the HNP surface and secondly, the use of a thermally labile linker. *In vitro* cytotoxicity studies combined with cellular uptake studies showed the formulations to be significantly more effective compared with gemcitabine (a nucleoside analogue marketed as Gemzar). *In vivo* trials have confirmed the *in vitro* findings that HNPs possess the ability to control drug release after heat initiation and significantly improve current cancer therapies.

COLL 382

Exploring nanoparticle architecture to design small, bright upconverting nanoparticles for bioimaging

Christopher Siefe¹, *csiefe@stanford.edu*, **Randy Mehlenbacher**², **Stefan Fischer**³, **Alice Lay**², **Jennifer Dionne**². (1) Materials Science & Engineering, Stanford University,

Stanford, California, United States (2) Stanford University, Stanford, California, United States

Imaging and understanding biological processes with high spatial resolution requires small optical sensors. Upconverting nanoparticles (UCNPs), which absorb low energy light and emit higher energy light, provide several advantages over other inorganic bioimaging probes including minimal autofluorescence background and enhanced photostability. Synthesizing small (sub 15 nm) and bright UCNPs remains challenging primarily due to 1) limited absorption due to the small quantity of absorbers and 2) surface quenching of the emission. To overcome these limitations, we tailor the nanoparticle architecture for maximum brightness. We compare two designs: a traditional core@shell design in which absorber and emitter ions are co-doped in the core and a novel core@shell@shell design where absorber and emitter ions are segregated into core and the first shell. These UCNPs consist of a hexagonal (*b*-) NaLnF₄ host lattice doped with absorber, Yb³⁺, and emitter, Er³⁺, ions. In both cases, the nanoparticles are passivated with an optically inert shell of *b*-NaLuF₄. Concentration of emitter ions (1, 2, 5, 10, 20, and 100% Er³⁺) and inert shell thickness (0-2 nm) are varied to determine the optimal architecture for bright UCNPs. In all cases, the UCNPs are maintained under 15 nm in diameter. We measured upconversion quantum yield, defined as the number of upconverted photons emitted divided by the number of absorbed photons, of ~0.1% for nanoparticles smaller than 15 nm in diameter for irradiances of 100 W/cm². Additionally, lifetime measurements of the absorptive and emissive states are used to understand the effect of the different UCNP architectures on the radiative and nonradiative relaxation rates. Finally, we probe single UCNPs using a confocal microscope setup to demonstrate single particle imaging and confirm our ensemble trends. Our studies reveal how doping concentrations in the homogeneous and heterogeneous configurations influence emission properties, thereby providing design principles for achieving smaller, brighter optical probes.

COLL 383

Design and surface engineering of upconversion nanoparticles for bioassays

*Markus Buchner, Verena Muhr, Sandy F. Himmelstoss, Lisa M. Wiesholler, **Thomas Hirsch**, thomas.hirsch@chemie.uni-r.de. Institute of Analytical Chemistry, Chemo- and Biosensors, University of Regensburg, Regensburg, Germany*

Upconversion nanoparticles (UCNPs) display exceptional material and luminescence properties for biological applications as donors in Förster resonance energy transfer (FRET) processes. Since FRET is strongly distance dependent, the diameter of the UCNPs and type of surface modification are expected to affect the FRET efficiency. A systematic study of the influence of the UCNP size on the energy transfer to organic dyes directly attached to the particle surface, acting as model FRET acceptors for the upconversion emission, revealed UCNPs with diameters in the range of 20 - 25 nm as the ones that yield the highest FRET efficiencies. Successful FRET was demonstrated through the drastic reduction of the lifetime of the respective upconversion emission.

Lower FRET efficiencies at both smaller and larger UCNP sizes were ascribed to an increasing competition of surface quenching and lower amounts of FRET donors within Förster distance to the acceptor dye on the particle surface, respectively. The insights gained from this systematical investigation of the impact of particle size on the FRET efficiency was the basis for the development of an efficient nanoprobe applicable for bioanalysis. Focus was put on smart particle design by combining the preparation of bright UCNPs facilitating high FRET efficiencies with proper surface engineering. Core-shell UCNPs of 25 nm diameter were synthesized, enabling enhanced upconversion emission intensity in an aqueous environment. Ligand exchange with polymers was identified as ideal intermediate layer for the subsequent attachment of biological receptors, representing the best compromise between intense upconversion emission, minimized donor-acceptor distance, colloidal stability and biocompatibility. Here, a structure switching adenosine triphosphate (ATP)-responsive aptamer was chosen as receptor. The aptamer-modified UCNPs were readily taken up by normal rat kidney cells (NRK) and did not show cytotoxic effects even at high particle concentrations. This probe design enabled the detection of physiologically relevant concentrations of ATP between 100 μ M and 1.0 mM. The comprehensive knowledge on the complex interplay between particle size and surface functionalization enables the development of enhanced FRET for an improved performance of UCNPs in bioanalytical and theranostic applications.

COLL 384

Mechanosensitive upconverting nanoparticles for visualizing mechanical forces *in vivo*

Alice Lay², alay@stanford.edu, Christopher Siefe¹, Stefan Fischer¹, Randy Mehlenbacher¹, Alakananda Das³, Adam Nekimken⁴, Feng Ke⁵, Wendy L. Mao⁵, Beth Pruitt^{4,6}, Bruce E. Cohen⁷, Paul Alivisatos⁸, Miriam Goodman³, Jennifer A. Dionne¹. (1) Materials Science & Engineering, Stanford University, Stanford, California, United States (2) Applied Physics, Stanford University, Stanford, California, United States (3) Molecular and Cellular Physiology, Stanford University, Stanford, California, United States (4) Mechanical Engineering, Stanford University, Stanford, California, United States (5) Geological Sciences, Stanford University, Stanford, California, United States (6) Bioengineering, Stanford University, Stanford, California, United States (7) Molecular Foundry 67R5110, LBNL, Berkeley, California, United States (8) University of California, Berkeley, Berkeley, California, United States

Mechanical forces influence many biological processes, including cell differentiation, muscle contraction, and disease. However, few sensors have the nanoscopic size or dynamic range to measure forces *in vivo*. Lanthanide-doped nanoparticles are an emerging class of optical probes due to their biocompatible features, including sharp emission peaks, high signal-to-noise, and photostability. In recent work, we found that cubic-phase (α) upconverting nanoparticles (UCNPs) are at least 2x more mechanosensitive than hexagonal-phase (β) UCNPs. Unfortunately, the centrosymmetric crystal field environment, which allows for high mechanosensitivity in

cubic-phase UCNPs, also contributes to their low quantum yield (QY).

In this work, we engineer brighter mechanosensitive core-shell UCNPs for biological applications. Sub-25 nm α -NaYF₄:Yb,Er cores are shelled with an optically-inert surface passivation layer of ~4.5 nm thickness. Using different shell materials, including NaGdF₄, NaYF₄ and NaLuF₄, we study how compressive to tensile strain, as confirmed by X-ray diffraction, influences the nanoparticles' imaging and sensing properties. All core-shell nanoparticles exhibit enhanced UCQY, up to 0.14% at 150 W/cm², which rivals the efficiency of unshelled hexagonal-phase nanoparticles. Using a diamond anvil cell, we perform in situ spectroscopy to characterize mechanosensitivity. Comparing shell types, the compressive NaGdF₄ results in the largest color response, from yellow-green to orange emission or quantitatively, $I_r/I_g = 12.2 \pm 1.2\%$ per GPa. All color responses consistent over three pressure cycles and stable for hours under near infrared illumination. For bio-compatibility, we modify the nanoparticle surface (e.g. ligand-strip, polymer-wrap) and further, monitor how pH and temperature influence optical properties. Finally, we demonstrate the first *in vivo* application of these UCNPs in the *C. elegans* pharynx. The worms are incubated with UCNPs overnight for feeding and then loaded in a microfluidic device for spectra collection. Based on ratiometric differences in emission peaks, we find that forces exerted in the grinder are nearly an order of magnitude higher than those exerted at the pharyngeal-intestinal valve.

COLL 385

Therapeutic modification of the tumor microenvironment to overcome intratumoral transport barriers for nanomedicine

Jayanth Panyam, jpanyam@umn.edu. *Pharmaceutics, University of Minnesota, Minneapolis, Minnesota, United States*

Nano drug carriers offer the potential for enhanced tumor drug accumulation. However, poor intra-tumoral penetration is a key limitation of these systems. Our recent studies show that lung and other solid tumors are characterized by extensive deposition of fibrin in the extracellular matrix (ECM). We hypothesize that modifying the tumor microenvironment using a fibrinolytic agent such as tissue plasminogen activator (tPA) will significantly improve nanomedicine penetration into otherwise inaccessible regions of the tumor and improve their therapeutic efficacy. In our studies utilizing a mouse model of human non-small cell lung carcinoma (NSCLC), co-administration of a fibrinolytic significantly improved the anticancer efficacy of nanoparticle-encapsulated paclitaxel. Co-treatment with tPA led to decompression of blood vessels and improved tumor perfusion. Further, treatment with tPA resulted in greater intratumoral penetration of a model nanocarrier (Doxil), leading to enhanced availability of the drug in the tumor core. Fibrinolytics such as tPA are already approved for other indications. Fibrinolytic cotherapy is therefore a rapidly translatable strategy for improving therapeutic effectiveness of anticancer nanomedicine.

COLL 386

Precision polymer architectures and molecular conjugates to enable therapeutics against undruggable targets

Craig Duvall, *craig.duvall@vanderbilt.edu*. Vanderbilt University, Nashville, Tennessee, United States

The Duvall Advanced Therapeutics Laboratory specializes in design and application of smart polymer-based technologies for: (1) intracellular delivery of biological drugs such as peptides and nucleic acids, (2) proximity-activated targeting of drugs to sites of inflammation and matrix remodeling, and (3) long-term, “on-demand” drug release from localized depots. These delivery systems are designed to improve the therapeutic index of existing drugs and/or to serve as enabling technologies for manipulation of intracellular targets currently considered to be “undruggable”. To achieve optimal, finely-tuned properties for these varied biomedical applications, polymers are utilized that respond to one or more environmental stimuli including pH, matrix metalloproteinases, reactive oxygen species, and temperature. This talk will focus on the latest nanoparticle and bioconjugate strategies from our group focused on development of new molecularly-targeted breast cancer therapies.

COLL 387

Controlling *in-vivo* fate of liposomes using a photocleavable PEG corona

Alexander Kros, *a.kros@chem.leidenuniv.nl*. Leiden University, Bodegraven, Netherlands

To prolong *in vivo* circulation times of drug delivery nano-systems, poly(ethylene glycol) (PEG) is often used to sterically shield nanoparticle surfaces. This serves to minimize adsorption of serum proteins to the nanoparticle and recognition and bodily clearance via the mononuclear phagocyte system (MPS). However, a PEG corona also inhibits interactions between nano-carriers and target cells, limiting drug delivery and effective therapy. To overcome this dilemma, cleavable PEG coronas have been developed to maintain long circulation lifetimes of nanoparticles while also achieving efficient cellular interactions with targeted cells. In this contribution, various strategies and examples of drug delivery systems with a sheddable PEG corona are presented.

Furthermore, we used embryonic zebrafish in order to track the distribution of nanomedicines in circulation upon intravenous injection, showing that *in vivo* distribution varies depending on the size and shape of these structures, the presence of a PEG corona and the effect of charge.

COLL 388

Multicompartmental nanoparticles for controlled release of combination therapies

Joerg Lahann, lahann@umich.edu. Univ of Michigan, Ann Arbor, Michigan, United States

Electrohydrodynamic co-jetting provides access to a wide range of multicompartamental nanoparticles where individual compartments can be loaded with different drug/matrix combinations to enable sequential release profiles. Examples include both synthetic polymers such as PLGA or PLC, as well as natural polymers including albumin and transferrin. To ensure effective tumor targeting, multicompartamental nanoparticles will be decorated with targeting molecules including peptides and single chain antibodies. Biodistribution, tumor targeting and efficacy of multicompartamental nanoparticles loaded with siRNA will be evaluated in the context of glioblastoma therapies. Systemically administered nanoparticles can effectively traverse the blood brain barrier and provide significant improvement of survival in a mouse model of glioblastoma.

COLL 389

Engineered lipid-antibody based nano-assemblies for painting and surface modifications of red blood cells for therapy of blood borne cancers

*Weston J. Smith¹, Lizanne G. Nilewski³, Nathan C. Gianneschi², **Dmitri Simberg¹**, dmitri.simberg@ucdenver.edu. (1) Pharmaceutical Sciences, University of Colorado, Aurora, Colorado, United States (2) Chem M/C 0343, University of California, San Diego, La Jolla, California, United States (3) Chemistry, Rice University, Houston, Texas, United States*

Many cancers are hallmarked by the presence of tumor cells in blood, for example circulating tumor cells in metastatic disease, or leukemic blasts in various blood cancers. There is a need in innovative tools for detection and eradication of these cells. We developed lipid-antibody based nano-assemblies for painting of red blood cells (erythrocytes) for cancer therapy. Using lipid antibody modified erythrocytes, we demonstrated targeting of various cancer cells and leukocytes in vivo. Furthermore, we demonstrated long-circulating properties of lipid-antibody modified erythrocytes. We will further describe the synthesis of novel amino indocyanine C18 antibody conjugates for advanced and more efficient cell painting. Anti-CD45 and anti-CD20 painted erythrocytes injected into mice were able to efficiently deplete leukemic cells in blood and peripheral organs, including bone marrow. Lipid antibody nano-assemblies are a promising tool for cell-based therapies.

COLL 390

Integrating synthetic protein chemistry and nanoparticles for intracellular delivery and targeted cancer therapy

***Ming Wang**, mingwang@iccas.ac.cn, Xiaoti Yang. Institute of Chemistry, Chinese Academy of Sciences, Beijing, China*

Protein is an expanding class of biotherapeutics with high potency to manipulate cell function and genetic information of cells for disease treatment. The low stability and cell penetration capability of proteins, however, challenges an efficient and effective protein therapy. In addition, new protein therapeutics that could be regulated and modulated by intracellular environment would allow the development of precision medicine for targeted disease treatment.

In this presentation, I will be talking about our recent research by integrating synthetic protein chemistry with nanotechnology for developing new generation of protein-based nanomedicine. The following two topics will be included: 1) we have developed several new chemical principles to modulate the cage and “de-cage” of cytotoxic protein, through which the protein shown “off-to-on” activity in response to tumor cell environment for targeted cancer therapy; 2) we have designed self-assembled nanoparticles, including combinatorial lipids and metal-organic nanoparticles to facilitate spatiotemporal protein delivery. The combined synthetic protein chemistry and nanotechnology are therefore of great potency for developing protein-based nanomedicine for advanced cancer therapy.

COLL 391

Neutrophil-based drug delivery systems

Zhenjia Wang, *zhenjia.wang@wsu.edu. Pharmaceutical Sciences, Washington State University, Spokane, Washington, United States*

White blood cells (WBCs) are an essential component of immunity in response to pathogen invasion. Neutrophils are the most abundant WBCs in humans, playing a central role in acute inflammation induced by pathogens. Neutrophil adhesion and tissue infiltration are key processes in acute inflammation. Many inflammatory/autoimmune disorders and cancer therapies have been found to be involved in activation and tissue infiltration of neutrophils. Here we report two types of neutrophil-based drug delivery systems: neutrophils as carriers and neutrophil membrane-derived nanovesicles. We will discuss how nanoparticles (NPs) hijack neutrophils *in vivo* to deliver therapeutics across blood vessel barriers and how neutrophil membrane-derived nanovesicles target inflamed vasculature. Finally, we will present the potential applications of neutrophil-based drug delivery systems in treating inflammation and cancers.

COLL 392

Tailoring renal clearance and tumor targeting of ultras-small metal nanoparticles with particle density

Shaoheng Tang¹, *tangshaoheng1@gmail.com*, **Jie Zheng**², **Chuanqi Peng**³, **Jing Xu**⁴, **Bujie Du**⁵, **Mengxiao Yu**⁶. (1) UTD, Dallas, Texas, United States (2) Chemistry, UT Dallas, Richardson, Texas, United States (3) Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, United States (4) Chemistry and Biochemistry, The

University of Texas at Dallas, Richardson, Texas, United States (5) Chemistry & Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States (6) University of Texas at Dallas, Richardson, Texas, United States

Identifying key factors that influence the behavior of nanomaterials is critical to the clinical translation of nanomedicines. Overshadowed by size-, shape-, and surface-chemistry effects, the impact of the particle core density on clearance and tumor targeting of inorganic nanoparticles (NPs) remains largely unknown. By utilizing a class of ultrasmall metal NPs with the same size and surface chemistry but different densities, we found that the renal-clearance efficiency exponentially increased in the early elimination phase while passive tumor targeting linearly decreased with a decrease in particle density. Moreover, lower-density NPs are more easily distributed in the body and have shorter retention times in highly permeable organs than higher-density NPs. The density-dependent behavior of metal NPs likely results from their distinct margination in laminar blood flow, which opens up a new path for precise control of nanomedicines in vivo.

COLL 393

Delivery of chemically modified siRNAs for human therapeutics: From principles to patients

Muthiah Manoharan, *mmanoharan@alnylam.com. Alnylam Pharmaceuticals Inc, Cambridge, Massachusetts, United States*

Synthetic small interfering RNAs (siRNAs) are potent inhibitors of gene expression through the RNA interference mechanism. The therapeutic potential of RNAi will be fully realized when these agents can be efficiently delivered into the cells of specific organs or tissues. At Alnylam, we have developed a three-pronged approach to enable efficient delivery of siRNAs into liver hepatocytes after either intravenous or subcutaneous injection. These methods include chemical modification of siRNAs, lipid nanoparticle formulation of siRNAs, and multivalent *N*-acetylgalactosamine (GalNAc) conjugation to siRNAs. Now, the potential of siRNA in treatment of “undruggable” diseases that was envisioned by the researchers is being realized. There are now several siRNA-based drugs in various stages of clinical testing and successful clinical results are emerging from these trials. The strategies and results will be discussed.

COLL 394

Attenuation of maladaptive responses in aortic adventitial fibroblasts through stimuli-triggered siRNA release from lipid-polymer nanocomplexes

Millicent O. Sullivan, *msullivan@udel.edu. University of Delaware, Newark, Delaware, United States*

Vascular bypass grafting is a routine treatment for cardiovascular diseases; however, ~50% of bypass grafts fail in the few years following surgery due to aberrant cellular responses at the suture sites. To address this problem, we recently focused on designing new and highly tunable light-based strategies to deploy nucleic acids with control at cellular length scales. Lipid-small interfering RNA (siRNA) complexes (lipoplexes) were modified with stimuli-responsive polymers to gain spatiotemporal control over gene knockdown in human primary aortic adventitial fibroblasts (AoAFs), which enabled the elucidation of the functional roles of IL1 β and CDH11 in improving vascular healing. Our previous work established the beneficial properties of our mPEG-*b*-poly(5-(3-(amino)propoxy)-2-nitrobenzyl methacrylate) [mPEG-*b*-P(APNBMA)] block copolymer system for vascular applications, including high stability and the capacity to locally regulate the extent of protein silencing on cellular length scales. Additionally, the precisely controlled nature of the system allows for accurate predictions of siRNA dosing regimens that facilitate gene knockdown over clinically-relevant timescales associated with adventitial remodeling (one week).

We exploited these characteristics through the formulation of hybrid nanocarriers that mediated on-demand, spatially-controlled knockdown of IL1 β and CDH11 in AoAFs to \leq 5% of their initial levels following treatment with a photo-stimulus. The silencing of IL1 β on its own significantly reduced myofibroblast differentiation and proliferation, whereas CDH11 silencing on its own had only a moderate effect. Subsequently, kinetic modeling approaches were used to design dosing regimens that fully silenced IL1 β and/or CDH11 together, over sustained time periods. Complete attenuation of TGF- β 1-induced myofibroblast differentiation was achieved by simultaneously silencing IL1 β and CDH11 for one week, the timescale relevant to adventitial remodeling. Thus, we uncovered synergistic functional roles of IL1 β and CDH11 in AoAFs and showed that sustained knockdown of these genes is a viable method for mitigating fibrotic responses. In the longer term, the photo-sensitive lipid-polymer nanocomplexes offer a unique opportunity to locally regulate fibrotic conditions and improve healing following cardiovascular surgery.

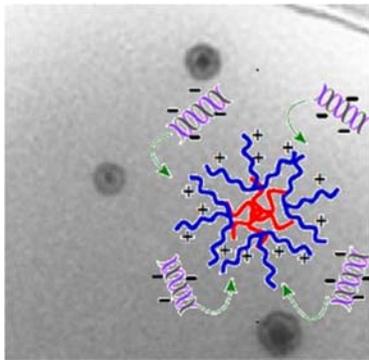
COLL 395

DyNAVectors: Dynamic constitutional vectors for adaptive DNA delivery

Mihai Barboiu^{1,2}, mihail-dumitru.barboiu@univ-montp2.fr. (1) *Institute European Membranes, Montpellier, France* (2) *Lehn Institute of Functional Materials, Sun Yat-sen University, Guangzhou, China*

Many functional platforms have been rationally designed with the hope of mimicking the complicated DNA histone machinery. The design of highly performant DNA vectors for efficient cellular uptake represents a grand challenge. However, DNA and target cells are highly variable and rational design is limited to a relatively small number of components. One possible solution to this problem is to employ the dynamic screening approaches. Herein, adaptive Dynamic Constitutional Frameworks, based on hydrophobic tails, polyethylene glycol and cationic heads components, which are

reversibly connected to core centers are combined and tested as DyNAVectors for DNA transfection. Depending on their tunable composition, these modular nanovectors dynamically self-adapt to their DNA targets, allowing the rapid screening of most effective vectors, optimally matched to DNA 3D surrounding space. Our strategy avoids complicate synthetic steps and allows easy and efficient identification of adaptive vectors with high DNA complexation ability, good transfection efficiency, and well tolerated by mammalian cells.



COLL 396

Induction of potent cytotoxic T-lymphocyte activity using two types of polysaccharides

Shinichi Mochizuki, mochizuki@kitakyu-u.ac.jp, Atsushi Moritaka, Kazuo Sakurai. The University of Kitakyushu, Fukuoka, Japan

Introduction: We have studied schizophyllan (SPG), a member of β -1,3-glucans, as a delivery carrier of oligo nucleotides since SPG can complex with particular homo nucleotides such as poly(dA). Furthermore SPG is recognized by We also a major β -1,3-glucan receptor Dectin-1 on immune cells such as macrophages and dendritic cells. In this study, we prepared CpG-DNA/SPG complexes and evaluated immune responses (CTL induction) *in vitro* and *in vivo*. We have also used hyaluronic acid (HA) as a delivery carrier to cancer cells. CTL attacks cancer cells with a cancer antigen on the cancer cell surface as a marker. However, some cancer cells spontaneously suppress the expression of cancer antigen that is essential for CTL recognition. In this study, to restore the CTL response for cancer cells, we prepared the conjugate consisting of HA and antigenic proteins and evaluate the CTL response.

Methods: We prepared CpG-dA₄₀ and made the complexes with SPG. After immunization with CpG-dA/SPG and antigenic protein OVA, we evaluated the immune responses to induce cytotoxic T lymphocytes (CTLs) and anti-tumor effect. A carboxylic group on HA was modified with OVA by a dehydration condensation reaction using EDC and NHS. We evaluated the immune responses after mixing of splenocytes immunized with OVA and melanoma cells treated with HA-OVA conjugate.

Results: Immunization with CpG-dA/SPG induced antigen specific immune

responses *in vitro* and *in vivo*. When splenocytes from immunized mice were incubated with E.G7-OVA tumor model cells presenting OVA peptides, the number of cells drastically decreased after 24 hours. Furthermore, mice pre-immunized with OVA and CpG-dA/SPG exhibited a long delay in tumor growth after tumour inoculation. The splenocytes mixed with melanoma cancer cells treated with HA-OVA conjugate secreted cytokines such as IFN- γ which shows Th1 type immune response. This result indicates that the replacement of weak antigenicity with strong antigenicity can be a novel strategy for cancer vaccine.

Conclusions: These findings indicate that the control of immune cells and cancer cells using SPG and HA may be expected to be next cancer and influenza vaccine.

COLL 397

Lymph node targeting of potent TLR7/8 agonist via acid sensitive amphiphilic polymers with high serum stability

*Bruno De Geest*¹, *Simon Van Herck*², *simon.vanherck@ugent.be*. (1) Ghent University, Ghent, Belgium (2) University Ghent, Gent, Belgium

Two key aspects take the highlight in developing anti-cancer vaccines, being the use of a vaccine adjuvant and the need for an efficient delivery system. Among all of the adjuvants, imidazoquinolines (IMDQ) have gained special attention as small molecule TLR 7/8 agonists. We and others have previously shown that covalent modification of an TLR 7/8 agonist to crosslinked nanoparticle leads to a strong localised immune activation in the draining lymph nodes. Here we report on a next generation of IMDQ-delivery systems based on novel amphiphilic block copolymers bearing a acid-cleavable benzylic moiety and an activated ester in the hydrophobic domain. The activated ester allows for post polymerisation functionalisation with an IMDQ derivative or fluorescent labelling. The benzylic moiety in the hydrophobic block promotes self-assembly into 50 nm micellar nanoparticles with increased stability due to π - π interactions. The use of an acid-sensitive ketal spacer allows the benzylic moiety to be cleaved of at lysosomal pH resulting in a fully water-soluble polymer that can present it's shielded TLR agonists. The concept of stable, but acid-degradable nanoparticles is shown in both an *in vitro* as well as *in vivo* setting based on Cy3/Cy5 FRET coupling. The lymphatic drainage was dramatically superior for the amphiphilic polymer compared to fully water-soluble polymer. Covalent modification of an IMDQ derivative to the micelle forming polymer yields a highly potent lymph node directing vaccine formulation with a strong localised immune activation.

COLL 398

Synthetic charge-invertible micelles for rapid and complete implantation of LbL drug films coated on microneedle patches for enhanced transdermal vaccination

Yanpu He^{2,3}, heyantu@mit.edu, **Celestine Hong**^{2,3}, **Jiahe Li**^{2,3}, **MayLin T. Funkenbusch**^{2,3}, **Yingzhong Li**^{1,3}, **Darrell J. Irvine**^{1,3}, **Paula T. Hammond**^{2,3}. (1) *Biological Engineering, MIT, Cambridge, Massachusetts, United States* (2) *Chemical Engineering, MIT, Cambridge, Massachusetts, United States* (3) *Koch Institute for Integrative Cancer Research, Cambridge, Massachusetts, United States*

Layer-by-layer (LbL) coated microneedle (MN) is a promising approach for transdermal drug delivery. One drawback of all state-of-the-art LbL MN strategies is the long epidermal application time (15-90 min) required for the drug coatings to detach from MN surface, which severely diminishes the attractiveness of such therapies. Here we developed a new release platform based on charge-invertible micelles requiring only 1-2 min skin insertion time to implant LbL film *in vivo*, faster than any other current method. Utilizing our new platform, we successfully implanted LbL film containing ovalbumin (OVA) antigen on mouse ear and achieved sustained release over 4 days. This has led to robust immune response compared to same amount of OVA injected subcutaneously and intramuscularly, as demonstrated by significantly higher anti-OVA IgG₁ antibody level in mouse serum. This work provides an easy and rapid LbL film implantation strategy for microneedle-based vaccinations.

COLL 399

R&D careers at Clorox: My experience from grad school to industrial career

Nancy A. Falk, nancy.falk@clorox.com. *Clorox Services Company, Pleasanton, California, United States*

The Clorox Company is an exciting place to start your industrial career. Our smart, values-driven people take pride in their work and their company. Our Research and Development (R&D) organization takes new generations of consumer products from concept to reality. With such diverse roles as engineers, scientists, mechanical designers and packaging experts, R&D is a community of technical leaders and managers actively involved in virtually every step in the lifecycle of our products, from initial concept to raw materials to final goods on store shelves. R&D is committed to leveraging the latest technology to bring consumers the high-quality, innovative products they expect and deserve. One of our R&D scientists will talk about the journey from grad school to a successful industrial career at Clorox and be happy to answer your questions. Clorox interviews at the ACS Fall National Meeting each year; if you are graduating or ending a postdoctoral fellowship in the 2018-2019 school year, we hope you'll consider interviewing with us at the Boston National Meeting. Read more about Clorox's college recruiting program at <https://www.thecloroxcompany.com/careers/college-recruiting/%234vZYAKKwxf5sWCQA.99>.

COLL 400

Careers in the startup environment

Billy Smith, *billysmith2526@gmail.com*. *Quality Control and Characterization, Nantero Inc, Woburn, Massachusetts, United States*

Joining the ranks of an industrial startup is a great way to exercise the skills learned from earning an advanced degree in science and engineering. In the startup environment, you have the opportunity to leverage your hard-earned laboratory skills, build management experience, significantly impact the organization, and foster relationships with foreign and domestic customers. One's ability to realize these opportunities will depend on the startup's business plan, however a major component to your success and career potential will be your personal drive and skillset diversity. These character traits, in addition to an advanced degree, are particularly important because startups thrive on a limited number of talented, highly committed individuals to achieve their organizational goals. While the experiential and potential financial opportunities afforded by the startup are tremendous, there is always the risk. To mitigate the risk, exercise due diligence when applying, and when you accept an offer and begin your career, always be prepared for the future by having a vision of what you want your resume to look like after two years of service. These are some of the lessons learned during my seven-year tenure at Nantero Inc, and I look forward to discussing the transition from graduate school to industry and answering your questions. Nantero is a mature nano-technology startup founded in 2001 and is the world leader in carbon nanotube electronics, developing a new generation of memory called NRAM® (non-volatile random access memory).

COLL 401

Emulsions with sustainable surfactants for personal care applications

Kathryn Whitaker¹, *kawhitaker@dow.com*, **Becky Beeson**², **Beth Johnson**³, **Carol E. Mohler**¹. (1) *Core R&D, Formulation Science, The Dow Chemical Company, Midland, Michigan, United States* (2) *Performance Silicones, The Dow Chemical Company, Midland, Michigan, United States* (3) *Home & Personal Care, The Dow Chemical Company, Midland, Michigan, United States*

As a leading chemical supplier, Dow is committed to delivering breakthrough sustainable chemical innovations to advance the well-being of humanity. Customers are also increasingly requesting "green" or sustainable products in a variety of areas, including personal care. Specifically the use of bio-based or renewable surfactants as emulsifiers is of interest for personal care applications such as beauty or hair care products. In this presentation a high throughput approach will be described which can accelerate the identification and selection of "green" surfactants as emulsifiers. Unique capabilities are leveraged to prepare emulsions and rapidly screen their key physical properties, such as particle size, sedimentation or creaming, rheology, and emulsion stability.

COLL 402

Chemistry and industrial careers

Anastasia Morfesis^{1,2}, ana.morfesis@malvern.com. (1) *Light Scattering and GPC, Malvern Panalytical, Westborough, Massachusetts, United States* (2) *Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States*

From specialty materials such as catalysts, coatings and composites to scientific instrumentation, I have had a diverse career in applied research. In general, I would say that chemists in industry must be flexible with a broad background and set of skills that allows them to continuously learn new fields. It is exciting to take new products from bench scale to production. On a large production scale, at thousands of pounds per hour or more, the statistics are such that the product either works or it doesn't. If the product has a problem it is a big one that must be solved quickly so that production can continue. Time is money where production is concerned.

On the other hand scientific instrumentation is a completely different scenario. This is a niche industry that primarily requires direct contact with clients from all over the world. The applications and problems that are brought to a scientist in this position span all industries. Application support in this industry is broad in nature, a scientist here, is not directly responsible for a final product/solution. However, the rigorous nature of this position is to identify new instrumentation that is capable of solving new problems for a significant percentage of clients.

Industrial or applied research can be ideal for the right candidate. It is interdisciplinary, requires team work and good interpersonal skills. A person that can learn quickly and finds it exciting to move between scientific fields will be most successful in this type of career.

COLL 403

Importance of surfaces and interfaces in government and industry R&D

Steven R. Carlo¹, steven.carlo@bep.gov, **Carissa M. Soto**¹, **Dennis H. Mayo**¹, **Brian T. Horlor**¹, **John M. Considine**², **David Allen**³. (1) *Materials and Applications Division, Bureau of Engraving and Printing, Washington, District of Columbia, United States* (2) *Forest Products Laboratory, Madison, Wisconsin, United States* (3) *Sensor Science Division, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, United States*

This presentation focuses on the importance and application of surfaces and interfaces to both industry and the United States government. The first part will focus on U.S. banknotes printed by the government's security printer, the Bureau of Engraving and Printing (BEP), and our collaborations with Forest Products Laboratory (FPL) and the National Institute of Standards and Technology (NIST). Dr. Carlo, who heads the

Materials and Applications Division, and his team are currently investigating the role of surface, chemical, and physical properties of U.S. banknotes using a variety of methods including contact angle, dynamic surface tension, X-Ray photoelectron spectroscopy (XPS), and micro-indentation; and at the macro level, the appearance and perception of banknote color. The second part will include a brief recap of some surface- and interface-intensive projects Dr. Carlo completed in prior industry positions and will touch on cosmetics development, structural failures, and consumer electronics. The final part of the presentation will include information and advice on obtaining internships and employment with the federal government.

COLL 404

Yes, HP Inc. is also a chemical company!

***Silke Courtenay**, silke.courtenay@hp.com. HP Inc, San Diego, California, United States*

HP Inc. is known for its computer and printer development, and has a long history of innovation. As one of the founding companies of The Silicon Valley, HP has a long tradition in engineering excellence. This is complemented by strong chemical R&D talent. HP holds thousands of patents in various chemistry applications such as: ink, paper, 3D, material science, and more. Our chemists have very diverse backgrounds and hold degrees in inorganic, organic, polymer, analytical, and material science, to name just a few. Our R&D labs have several options for exciting careers with growth opportunities, in both our technical career path, and in technical management. The chemical science R&D at HP builds the innovation foundation for all of our product development. One of our R&D chemists will talk about a few of the numerous different chemistry applications that we have at HP, and the exciting careers that HP offers in the chemical fields.



COLL 405

LINX: Linking industry to neutrons & X-rays

***Gregory Smith**, gregoryneil@gmail.com, Erik Brok, Martin Schmiele, Lise Arleth, Kell Mortensen. Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark*

Neutron and X-ray techniques have a huge potential for solving technological problems for the benefit of society. However, while scattering techniques have long been invaluable tools for academic research, the techniques employed at modern large-scale

facilities are highly specialized and most companies do not have the expertise to take advantage of the opportunities.

Following the large public investment in the European Spallation Source (ESS) the Danish government, through Innovation Fund Denmark, have invested in the LINX Project. The goal is to help Danish industry benefit from the ESS neutron source and the MAX IV X-ray synchrotron. LINX is a network of three Danish universities, with expertise in neutron and X-ray methods, and many industrial companies, encompassing a diverse set of applied science. This includes a focus area on Colloid Materials with projects on a range of industrial problems from a range of colloid and interface science.

The university scientists help the industrial partners identify problems, which can be addressed with neutron and X-ray techniques, and they then work with them to design suitable experiments, acquire beam time, performing measurements, and analyze data.

The overall goal of LINX is to establish a strong organization that can help industry gain short and long-term technological advances and develop new capabilities in neutron and X-ray techniques. It is our hope that an expanding user community of industrial colloid scientists will help push for developments in research infrastructure, instrumentation, and sample environments to the benefit of the neutron and X-ray communities. I will discuss the operation of the LINX organization and show examples of how we use neutron and X-ray scattering to solve industrial problems.

COLL 406

Applications of surface chemistry in the cosmetic industry

Hy S. Bui¹, hbui@rd.us.loreal.com, Gustavo S. Luengo². (1) Loreal, Clark, New Jersey, United States (2) Loreal Research, Aulnay Sous Bois, France

A great diversity of materials is used to protect or improve the structural and sensorial properties of surfaces (hair, skin, nail...). From shampoos to lacquers or gels, materials are commonly used to perform a particular function (mechanical, optical, etc.) upon adsorption and/or penetration in the fiber or either after a particular change in an external condition that may trigger its activation (temperature, weathering, etc.).

Knowledge of the structure and nature of the substrate is essential if we want to clearly determine the degree of improvement of its physical properties. This description will be further illustrated with a few examples of our current research efforts deciphering the physical chemical properties of hair at the bulk and surface level and at the macro, micro and sub-microscopic scale.

As an example of common surface modifications of the cosmetic substrate, we will describe the nature and properties of polymers commonly used in shampoos and conditioners. Alternatively, in the case of fiber reinforcing materials, we will also explain our recent strategies that modify the mechanical nature. Finally, we will present

examples of rheological behavior of gel formulations present in common products as a result of its degree of micro-structuration. Our examples will show how materials can be effectively tuned to the consumer's advantage and show how to put in practice some of the basic principles we learnt from graduate school.

COLL 407

Colloid and surface science in Cabot R&D

Ani T. Nikova, *ani.nikova@cabotcorp.com. Cabot Corporation, Billerica, Massachusetts, United States*

Cabot Corporation is a global specialty chemicals and performance materials company. In addition to offering a broad portfolio of particle solutions, we work closely with our customers to solve complex materials problems. We do this by leveraging our competencies in material science, surface engineering, characterization, and application expertise to find solutions that provide performance, and break functional trade-offs. Our R&D people are driven and inventive, and they come from backgrounds in chemical and mechanical engineering, materials science and chemistry. In this talk, examples will be given from R&D activities at Cabot relevant to colloid science. One example is on characterization of fine particles and linkage of materials properties to desired applications. Another project is on development of materials for aqueous inkjet inks for improved optical density on paper. Our R&D scientist will be happy to answer questions on career paths and industrial research at Cabot.

COLL 408

Functional polycarbonate materials: Synthesis, modification, and application

Nathan Park, *npark@us.ibm.com. IBM Research, San Jose, California, United States*

Aliphatic polycarbonates have numerous applications in biomedical science. Here we discuss strategies for their selective synthesis and post-synthesis modification. These approaches enable a broad spectrum of biomedical applications, including use for treatment of infectious disease and cancer. The relation of polymer structure to these biological functions will be discussed.

COLL 409

Mussel-inspired silicone oil swelling slippery surfaces with repeatable wettability recovering under extreme operating conditions

Biyu Jin, *jimmyjin@zju.edu.cn, Qinghua Zhang, Xiaoli Zhan, Fengqiu Chen. Zhejiang University, Hangzhou, China*

Slippery liquid-infused porous surfaces (SLIPS) have attracted widespread attention due to its exceptional surface properties. However, the Achilles' heel of SLIPS still remains unsolved that once the substrates destroyed by external force, it would not be good reservoir for lubricant storage. Albeit surface wettability recovering of damaged areas can be achieved temporarily, lifetime-long functionalities will be snatched away eventually with rapid lubricant losing. In this work, a novel substrate building block, magnetic Fe_3O_4 nanoparticles armed with dopamine molecules were developed via mussel-inspired metal-cation coordination bonds. Combined with glycidyl methacrylate, polydimethylsiloxane propyl ether methacrylate, and diethylenetriamine, the original silicone oil swelling slippery liquid-infused porous surfaces were first prepared by reversible coordinate bonds and strong covalent bonds cross-linking process. Results show that the mechanical property of copolymer matrix and surface wettability of SLIPS can be remarkably recovered, which were due to the synergistic interactions of magnetic nanoparticles' intrinsic photothermal effect, reversible Fe-catechol coordination, and diffused lubricating liquid. After irradiating with sunlamp for 2 h and sequentially heating for 10 h under ambient conditions, the crack almost disappeared under optical microscopy with 78.25% healing efficiency (HEf) of toughness, and surface slippery was completely retrieved to water droplets. Moreover, the prepared SLIPS displayed superb self-cleaning and liquid-repellent properties to a wide range of particulate contaminants and fluids.

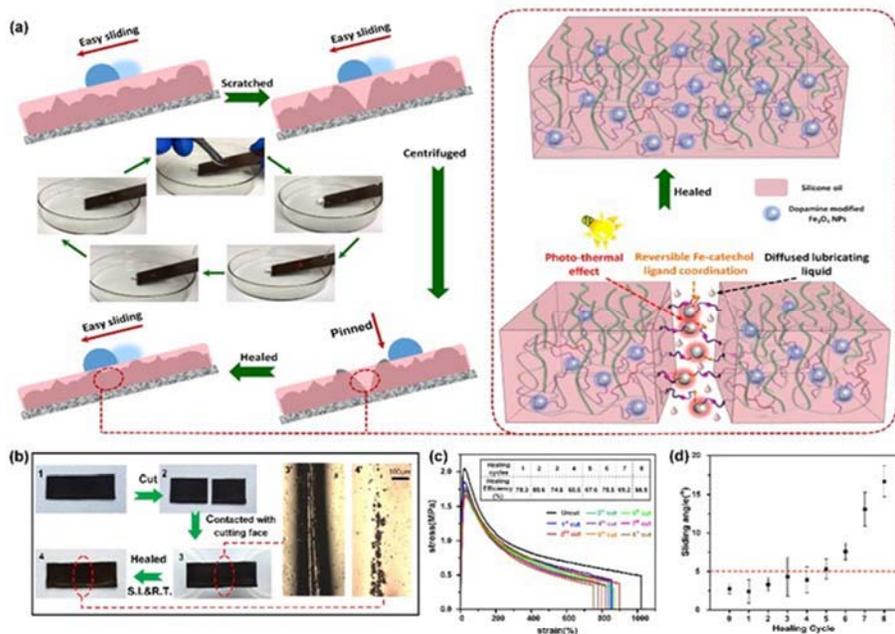


Figure 1. (a) Schematic illustration and images of surface wettability recovering ; (b) Self-healing process of PG-MNP15; the original undamaged material (1) was cut into two pieces (2), then could stand on two lids after adjoining the pieces at interface for 10 min (3) and sample after 2 h sunlamp irradiation (S.I.) followed by 10 h room temperature (R.T.) healing process (4). (3') and (4') are optical microscope images of b3 and b4's incisions; (c) stress-strain plots of PG-MNP15 samples experienced 1 to 8 times cutting-healing cycles respectively; (d) Sliding angles of SPG-MNP15 versus cutting-centrifuging-healing cycles.

COLL 410

Peptide adsorption on hydroxyapatite surfaces and implications on shape and mineralization: Impact of sequence and electrolyte pH

Juan Liu¹, Samuel Edmund Hoff¹, samuel.hoff@colorado.edu, Chandrani Pramanik², Tariq Jamil³, Sara Kay VanOosten⁴, Kyle Boone⁴, Candan Tamerler⁴, Hendrik Heinz⁵. (1) Colorado University of Boulder, Boulder, Colorado, United States (2) Materials Science, Georgia Institute of Technology, Atlanta, Georgia, United States (3) Polymer Engineering Department, University of Akron, Akron, Ohio, United States (4) The University of Kansas, Lawrence, Kansas, United States (5) Dept of Polymer Engineering, University of Akron, Akron, Ohio, United States

Hydroxyapatite (HAP) is a common calcium phosphate phase in teeth and bone, however, details of its formation and dissolution have remained difficult to understand in atomic detail. In biomimetic laboratory synthesis, the peptide sequence MLPHHGA (HABP1) derived from phage display leads to the formation of plate-like HAP nanocrystals at pH 7 with a lower initial nucleation rate compared to using no peptides or a control sequence NPGFAQA (HABP2) that is not active in binding and mineralization. Recent developments of accurate apatite models in the Interface force field (IFF) allow pH sensitive simulations of mineral precursors, nanocrystals, and biointerfaces (CHARMM-IFF, AMBER-IFF) in atomic resolution. Here we describe the molecular interaction of HABP1 and HABP2 with apatite surfaces at pH values of 5, 7, and 10 for all common crystal surfaces including the (001) basal plane, the prismatic (010) and (020) surfaces, as well as (101) surfaces at the tip of HAP crystallites. HABP1 shows much stronger adsorption on the HAP (101) and (020) surfaces compared to (001) and (010) surfaces, consistent with a higher growth rate along the [001] direction observed in experiment. HABP1 in solution also shows a high affinity to calcium ions which is likely to slow down the nucleation rate of hydrogen phosphate precursors to form apatite. The differences in the computed adsorption free energy of HABP1 on each facet of HAP are consistent with the observed of plate-like morphology in experiment at pH 7, and specific to the chosen pH value. The control peptide sequence NPGFAQA (HABP2) does not exhibit strong binding performance to any facet of HAP, and neither a strong affinity to calcium ions in solution, which is in good agreement with the experimental observation of a sphere-like morphology of biomimetically grown HAP and a higher initial nucleation rate. The findings show that the new molecular models and simulations using CHARMM-IFF are of predictive quality and can be used for rational biomaterials design.

COLL 411

Multifunctional macroporous biomaterial for drug delivery and efficient emulsion separations

Ananta Ghimire¹, ananta.ghimire@uconn.edu, Dennis Ndaya¹, Rajeswari Kasi², Challa V. Kumar³. (1) University of Connecticut, Storrs, Connecticut, United States (3) Univ of Connecticut, Storrs Mansfield, Connecticut, United States

A highly porous protein-based material (sponge) for efficient separation of oil-in-water emulsions is presented here. The sponge was synthesized by covalent crosslinking between the protein molecules by carbodiimide chemistry and it showed excellent hydrophilicity as well as oleophobicity. The sponge exhibited unusual shape memory (100% shape recovery) and it was able to separate surfactant-free and surfactant-stabilized oil-in-water emulsions into the aqueous and oil phases with high efficiency (99.1%) and rapidity (few minutes). In addition, the sponge showed robust mechanical properties and without significant plastic deformation after compression for 50 cycles. The protein sponge is ideal for bio-implantation and non-toxic drug delivery, and these applications will be discussed.

COLL 412

Binding nanomaterials to living bacteria

Hong Dong^{1,2}, dong.rena@gmail.com, Deborah A. Sarkes¹, Jessica Terrell¹, Justin P. Jahnke¹, Margaret Hurley¹, Dimitra Stratis-Cullum¹. (1) US Army Research Laboratory, Adelphi, Maryland, United States (2) General Technical Services, Wall, New Jersey, United States

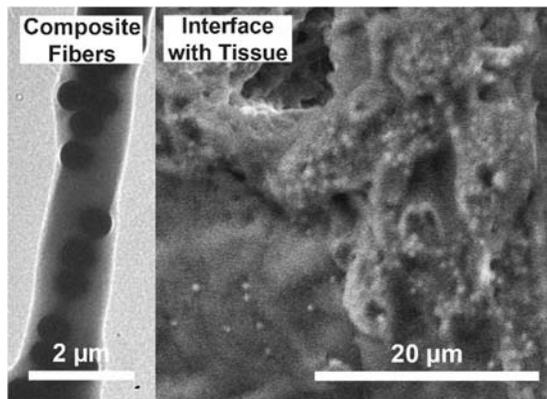
The ability to control the interaction between bacteria and nanomaterials is fundamental for creating living hybrid systems as well as pathogen anti-adhesion. In this talk, we will discuss our work in tuning the bio/abio interfacial interactions for binding of nanomaterials to living bacteria either through genetic engineering or through nanomaterial functionalization. In the first study, living bacteria/nanoparticle hybrids were prepared by genetically controlling binding peptide displayed on bacterial surfaces. *Escherichia coli* (*E. coli*) was engineered with inducible gene circuits to control display of peptides on bacteria with desired sequences. Driven by metal-peptide affinity, nanoparticles such as gold or magnetic nanoparticles could self-assemble onto the bacteria with programmed peptides. The bacteria/nanoparticle hybrids were highly viable and maintained the ability to grow and divide. Potential applications of the living bacteria/nanoparticle systems will be briefly discussed. In the second study, cellulose nanofibrils, a biocompatible and easily modified nanomaterial platform, were functionalized with mannose to be used as a new tool in the control of bacterial pathogenesis. The functionalized nanofibrils were capable of regulating of *E. coli* association due to strong affinity between multivalent mannose grafted on nanofibrils and receptors on *E. coli*. These bioactive nanofibrils demonstrated the ability of capturing *E. coli* as well as preventing adhesion of *E. coli*.

Incorporating silica particles improves the adhesion, flexibility, and hemostatic efficacy of a polymer blend surgical sealant

John L. Daristotle¹, jldaristotle@msn.com, Shadden T. Zaki², Leopoldo Torres Jr¹, Lung W. Lau³, Aristotelis Zografos², Omar B. Ayyub⁴, Anthony D. Sandler³, Peter Kofinas⁴. (1) Fischell Department of Bioengineering, University of Maryland, College Park, Maryland, United States (2) Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States (3) Sheikh Zayed Institute for Pediatric Surgical Innovation, Joseph E. Robert Jr. Center for Surgical Care, Children's National Medical Center, Washington, District of Columbia, United States (4) Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland, United States

Surgical sealants are supplements to conventional wound closure devices that augment hemostasis and may reduce complication rate. However, commercially available surgical sealants adhere poorly to wet tissue and are difficult to apply precisely. Here, solution blow spinning (SBS) serves as a sprayable deposition method for easily depositing conformal surgical sealants directly to the wound. The objective of this research is to increase tissue adhesion by incorporating nano-to-microscale particles into a poly(lactic-co-glycolic) acid and poly(ethylene glycol) blend sealant (PLGA/PEG) whose deposition is compatible with SBS. Our experiments focus on understanding how the silica particles interact at the interface with tissue, measuring adhesive interactions, and determining possible mechanisms for adhesion improvement which may be of broader interest to the field of surface science.

Adhesion increases dramatically by incorporating silica particles into the PLGA/PEG blend surgical sealant, but does not cause a significant decrease in cell viability. Composite PLGA/PEG/SiO₂ sealants produce intestinal burst pressures that are comparable to cyanoacrylate glue (156 mmHg), ~2 times greater than PLGA/PEG (59 mmHg), and ~3 times greater than fibrin glue (48.6 mmHg). Adhesive force increases by 20% while adhesion energy, which takes into account work dissipated by the bulk of the sealant, is 20 times higher. Scanning electron microscopy shows silica particles sandwiched at the interface between tissue and sealant, where they create dense networks of physical bonds. Cytotoxicity studies show no significant differences between PLGA/PEG and composite sealants. Coagulation time of whole blood exposed to the composite sealant decreases compared to PLGA/PEG alone. These improvements demonstrate the potential of a simple composite design to increase adhesion through physical, noncovalent mechanisms.



COLL 414

Nanogels of zwitterionic polymer-curcumin conjugates function as a potent inhibitor of amyloid β -protein fibrillogenesis and cytotoxicity

Guangfu Zhao, Xiaoyan Dong, Yan Sun, ysun@tju.edu.cn. Department of Biochemical Engineering, Tianjin University, Tianjin, China

Aggregation of amyloid β -protein ($A\beta$) on neuronal cells is a pathological hallmark of Alzheimer's disease (AD), so inhibition of $A\beta$ aggregation is an preferred strategy for the precaution and treatment of AD. Previous studies indicate that curcumin inhibits $A\beta$ fibrillogenesis and alleviates its associated cytotoxicity. However, owing to its poor solubility, the therapeutic efficacy of curcumin has been greatly limited. In order to improve its bioavailability, curcumin was conjugated to a zwitterionic polymer, poly(carboxybetaine methacrylate) (pCB), and the conjugates, Cur@pCB, self-assembled into nanogels. The inhibitory activity of Cur@pCB on the aggregation and cytotoxicity of both $A\beta$ 1-40 and $A\beta$ 1-42 was investigated. It was found that the Cur@pCB was much more efficient than free curcumin at equivalent curcumin concentrations. It greatly decreased the amyloid aggregation as detected by thioflavin T fluorescence, retarded the conformational transition of the amyloid proteins, changed the aggregates' morphology, and thus protected the cultured cells from the toxicity of the amyloids to the same viability at only about 1/5 of free curcumin concentration (5 vs. 25 $\mu\text{mol/L}$). On the basis of the experimental findings, a mechanistic model was proposed. It is considered that, besides the inhibition effect of curcumin itself, the dense hydration layer on pCB would strongly interfere with the bound $A\beta$ molecules on the conjugated curcumin, suppressing the conformational transition of the protein to β -sheet-rich structures. This work offered new insights into the development of potent nanogels for suppressing $A\beta$ fibrillogenesis and cytotoxicity.

COLL 415

Three ways of fine-tuning cell adhesion to synthetic surfaces

Joseph B. Schlenoff, *schlen@chem.fsu.edu*, **Richard Surmaitis**, **David Delgado**, **Carlos Arias**. *Florida State Univ, Tallahassee, Florida, United States*

The toolbox of methods to control interactions of cells with surfaces has been growing in recent years. In some cases, highly specific interactions are programmed to encourage adhesion of a cell type. In other cases, interactions are less specific, with the goal of generally promoting or preventing cell adhesion. This presentation will focus on three molecular strategies for controlling cell adhesion. First, the success of zwitterion moieties in defeating cell and protein adhesion will be rationalized, with examples of planar and nanoparticle surfaces. Second, the strength of cell-protein interactions will be shown to depend on the chemical nature of the surface charge, yielding cytophobic to cytophilic response. Finally, an engineered ultrathin film presenting thiol functionality, and the broad selection of chemical and physical properties that comes with this functional group, will be discussed. In all examples, fundamental understanding of the mechanisms of action will be explored.

COLL 416

kT-scale interactions between zwitterionic coated colloids and biomaterial surfaces

Michael A. Bevan, *mabevan@gmail.com*. *221 Maryland Hall, Johns Hopkins Univ Chemistry Biomol Engr, Baltimore, Maryland, United States*

Zwitterionic polymer coatings have recently gained attention in biomaterial and environmental applications, with several studies claiming improvements in surface stabilization and antifouling relative to more traditional polymer chemistries like poly (ethylene oxide) (PEO). Here we report measurements of zwitterionic copolymer coated colloids interacting with a variety of biomaterial surfaces including adsorbed protein, lipid, mucus, extra cellular matrix, and cell surfaces. Relative to PEO, zwitterionic polymer brushes stabilize colloidal particles with a fraction of the repeat units, a result of an enhanced chain extension. Mechanisms for this extension are discussed for two zwitterionic monomers, with studies of monomer-monomer and monomer-solvent interactions. Finally, we conclude with a study of colloidal interactions and stability between zwitterionic brushes and several biomaterial systems (can we say anything more about results here?). These studies demonstrate that brush thickness--not monomer chemistry--is the dominant factor in determining the performance of a polymer coating, and offer a mechanistic explanation for the stabilization behavior reported in the literature.

COLL 417

Protein encapsulation using cationic copolymers in the presence of zwitterionic surfactants

*Amir Erfani, Nicholas H. Flynn, Josh D. Ramsey, **Clint Aichele**,
clint.aichele@okstate.edu. Chemical Engineering, Oklahoma State University,
Stillwater, Oklahoma, United States*

Protein encapsulation using cationic polymers is one of the methods that is being studied for forming nano size protein delivery vehicles. In designing an efficient drug carrier, many functions such as release capabilities, cell penetration, protein content per each carrier, and high efficiency of encapsulation need to be controlled. Surfactants are known to be penetration and permeation enhancers and show the most potential when integrated into a localized delivery. Furthermore, surfactants are known to lower the critical aggregate concentration of polymers. While the use of surfactants has been studied in micro-encapsulation, here, the effect of the surfactants is studied in the nano scale encapsulation of Bovine Serum Albumin (BSA) as a model protein. To achieve this, encapsulation of BSA, with polyethylene glycol grafted polylysine is carried out in the presence of a zwitterionic surfactant. A gel electrophoresis method is used to determine the extent of BSA encapsulation. The method is based on the difference in mobility of encapsulated and free proteins. Furthermore, the ability of the proposed vehicle to control release, co-encapsulation, and minimizing the effect of the ionic strength on encapsulation performance are studied. Moreover, design of a better therapeutic vehicle is only possible when the interactions between the components are understood. For this purpose, diffusion Nuclear Magnetic Resonance (NMR) spectroscopy is utilized to study the interactions that can affect the efficiency of the proposed drug delivery vehicle. The self-diffusion of the components is utilized as the criteria for determining the surfactant Critical Micelle Concentration (CMC) and the polymer aggregation concentration in the presence of surfactant. Results of this study help to elucidate the protein-polymer and protein-surfactant interactions.

COLL 418

Removal of silica from oil-sands produced water by electrocoagulation

***Edward Roberts**, edward.roberts@ucalgary.ca, Behzad Fuladpanjeh-Hojaghan, Tiapei Shu, Nael Yasri, Milana Trifkovic. University Calgary, Calgary, Alberta, Canada*

Electrocoagulation is a cost effective separation technology for removal of organic and inorganic contaminants from water. However, the mechanism of contaminant removal and operational challenges such as electrode fouling have limited widespread application. In this study we examine the influence of the electrode boundary layer on the contaminant removal and electrode fouling processes, with silica removal from produced water as the target application. Bench scale testing has demonstrated the effectiveness of electrocoagulation for the removal of silica from the produced water with minimal electrical energy consumption. However, electrode fouling remains an important challenge. To study the electrode boundary layer, we developed a method using pH sensitive fluorescent dyes and laser scanning confocal microscopy (LSCM) to visualise the pH distribution close to the electrodes. Using ratiometric analysis the pH distribution can be mapped in space and time. Acidic conditions are observed close to

the anode, due to hydrolysis reactions as metal ions are dissolved into solution, as well as proton generation associated with oxygen evolution. The pH at the electrode surface can be 2 or more pH units lower than the bulk. At the cathode, strongly alkaline conditions can be observed, as hydroxide ions are generated from the hydrogen evolution reaction. These pH boundary layers influence the coagulation processes through hydrolysis reactions in the anode boundary layer, and thus play an important role in the separation process. Furthermore, the rate of deposition of precipitates at the electrode surface will also be a function of the local pH at each electrode. This study thus provides new insights into contaminant removal and fouling processes in electrocoagulation. We have also investigated the use of polarity reversal to control electrode fouling. Polarity reversal leads to rapid pH swings at the electrode surface, which enables reduction in the fouling but also influences the coagulation processes. The particle size distribution of precipitated coagulant changes depending on the frequency of the reversal. At high frequency there is less electrode fouling, but the particle size formed is smaller, so separation of the solids becomes more challenging.

COLL 419

Unconventional interfacial reactivity of metal sulfides: Relation to mineral separation

Hanumantha R. Kota, hanumantha.rao.kota@ntnu.no. Geoscience and Petroleum, Norwegian University of Science and Technology, Trondheim, Norway

It is a classical long-standing industrial problem to separate ferrous from non-ferrous metal sulphides, which is mainly done by froth flotation. This method is based on the differences in the surface chemistry of minerals. Therefore, most of the research in this area focuses on the understanding of the selective interactions of metal sulfides with surfactants. In contrast, we found that these minerals have catalytic activity and generate reactive oxygen species and hydrogen peroxide (H_2O_2), which can modify their interaction with surfactants. We studied the formation of hydrogen peroxide by sulfide minerals during grinding. It was found that pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS), which are the most abundant sulfide minerals on Earth, generate hydrogen peroxide during wet grinding in the presence and absence of dissolved oxygen in water and also when the freshly ground solids are placed in water immediately after dry grinding. I will present these results highlighting the necessity of revisiting the electrochemical and/or galvanic interactions between the grinding medium and sulphide minerals, and interaction mechanisms between pyrite and other sulphide minerals in terms of their flotation behaviour, leaching and environmental degradation in the context of inevitable hydrogen peroxide presence in aqueous suspensions of metal sulphides.

COLL 420

Silica supported sterically hindered amines for CO_2 capture

Jason Lee¹, jlee3095@gatech.edu, **Chunjae Yoo**¹, **Chia-Hsin Chen**², **Sophia E. Hayes**², **Carsten Sievers**¹, **Christopher W. Jones**¹. (1) *Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States* (2) *Department of Chemistry, Washington University, Saint Louis, Missouri, United States*

Solid supported amines are promising materials for the separation of CO₂ from dilute sources such as ambient air and flue gas. Most studies exploring the capture of CO₂ on solid supported amines have focused on simple, sterically unhindered amines or alkyimine polymers. It is observed in extensive solution studies that another class of amines, namely sterically hindered amines, can give enhanced CO₂ capacity when compared to their unhindered counterparts. While sterically hindered amines have been well studied in solution, there has been limited research conducted on this class of amines on solid supports.

In this work, one hindered primary amine and two hindered secondary amines are functionalized onto mesoporous silica at similar amine coverages and their CO₂ adsorption performances are investigated using fixed bed breakthrough analysis. Furthermore, chemisorbed CO₂ species formed on the sorbents under dry and humid conditions are elucidated using *in situ* FTIR spectroscopy. Enhancement of CO₂ adsorption capacity is observed for all supported hindered amines under humid conditions and this increase in capacity is mainly due to the formation of ammonium bicarbonates. Our experiments also suggest that chemisorbed CO₂ species formed on supported hindered amines are weakly bound, which may lead to reduced energy costs associated with regeneration.

COLL 421

Novel conducting composites for enhanced separation of salt from brackish water

Sathish Ponnurangam¹, sathish.ponnurangam@ucalgary.ca, **Chengying Ai**¹, **Viola I. Birss**². (1) *Chemical and Petroleum Eng, University of Calgary, Calgary, Alberta, Canada* (2) *Univ of Calgary Chem Dept, Calgary, Alberta, Canada*

Membrane fouling and energy consumption are two key factors that make membrane-based separation processes (e.g., reverse osmosis) for removing salt from brackish water very expensive. An emerging method, capacitive deionization (CDI), can be both membrane-free and low in energy cost. In CDI, salt is removed by applying an electric potential across porous electrodes in brackish water. This polarization results in electrosorption of counter ions in the electrical double layer of the electrodes. One of the limitations that hinder widespread application of CDI is the low capacitance of carbon electrodes, which necessitates a large surface area. In this work, we report a novel nanocomposite that exhibits highly enhanced capacitance (3-6 times) compared to a typical porous carbon electrode. Our nanocomposite electrode is based on the use of a hierarchical porous carbon scaffold and a conductive polymer (polyaniline). We describe strategies to control the morphology of polyaniline grown on the carbon scaffold surface that maximizes the capacitance without clogging the pores of the carbon. Our

nanocomposite is robust, since it has retained its capacitance at ~95% even after 10 charge-discharge cycles and offers a great potential as a CDI electrode.

COLL 422

Redox interfaces for electrochemically-mediated separations of heavy metal contaminants

Xiao Su, x2su@mit.edu, T. Alan Hatton. Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Electrochemically-responsive interfaces have become an integral part of surface chemistry and colloids science research, for applications ranging from energy storage to environmental processes. In particular, adsorption-based electrochemical methods have recently shown great promise for desalination, due to their modularity and reusability. However, their implementation for selective ion recovery and water purification remains limited by lack of specificity of the electrode materials, and relatively high energetic costs.

Redox-functionalized electrodes offer an attractive platform for performing selective electrochemical separations based on their remarkable ion binding capabilities. In particular, redox-metallopolymers interfaces have shown remarkable capabilities for selective sorption and release of organic contaminants, and even proteins, based solely on electrochemical control. Here, we present for the first time the capabilities of redox-electrodes for the selective sorption of a range of transition metal contaminants, including chromium species. Hexavalent chromium, in particular, is one of the most prevalent pollutants in both urban and agricultural waters, and is usually present in anionic form. With our redox-electrodes, a molecular uptake of greater than 100 mg Cr/g adsorbent can be achieved, with a reversible working capacity of more than 99% controlled solely by electrochemical potential. We also discuss the merits of pursuing asymmetric electrochemical design to reduce voltage windows and energetic costs, and the extension of the current technologies for a wider range of heavy metal contaminants. Finally, we present nanoscale investigations of our electrochemical interfaces during ion adsorption and polymeric swelling, through advanced in-situ imaging.

From a fundamental perspective, our concepts point towards an emerging direction in electrochemical interface design – by superimposing properly tuned chemical interactions, we can reach beyond double-layer effects and achieve highly selective ion separations. From a practical perspective, these findings are expected to demonstrate electrochemical technologies as a sustainable path for both water purification and environmental remediation.

COLL 423

Controlling selectivity on metal nanoparticles with organic monolayers

James W. Medlin, *will.medlin@colorado.edu*. Chem. Biol. Eng UCB 596, University of Colorado, Boulder, Colorado, United States

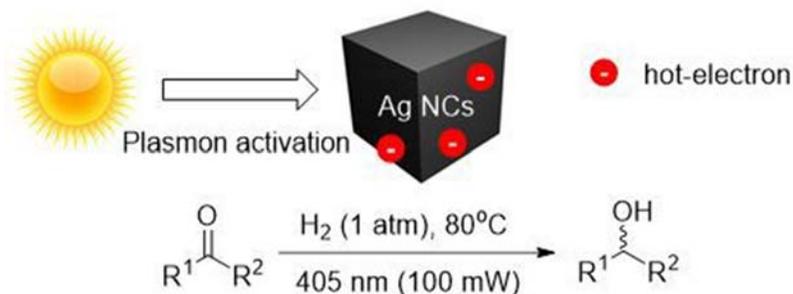
Organic ligands are frequently used in the preparation of metal nanoparticles of controlled size, shape, or composition. These coatings have typically been considered to be undesirable from the standpoint of catalytic properties. However, tuning of the molecular structure of the organic ligands has the potential to influence interactions between reactants and the metal surface, allowing one to use it as a lever to control selectivity. This presentation will focus on recent efforts to engineer organic coatings to improve the selectivity of heterogeneous catalytic processes. Perhaps more surprisingly, these coatings can also significantly improve catalyst activity and stability, as will be discussed through multiple examples.

COLL 424

Plasmonic catalysis as a means for sustainable transformations

Audrey H. Moores¹, *audrey.moores@mcgill.ca*, **Michael J. Landry**², **Alexandra Gelle**², **Christopher J. Barrett**³. (1) Chem Dept, McGill University, Montreal, Quebec, Canada (2) Chemistry, McGill University, Montreal, Quebec, Canada (3) McGill University, Montréal, Quebec, Canada

Plasmonic materials are metal-based nanoparticles featuring strong absorption properties arising from the oscillation of their conducting electrons. They have recently attracted the attention of the catalysis community and been exploited to activate small molecules. Silver nanocubes have been used by Linic and coworkers to catalyze epoxidation reactions, and Halas and coworkers to assist hydrogenation reactions. We have employed silver nanocubes for the activation of H₂ and hydrogenate ketones and aldehydes at 1 atm. Upon irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes, the reaction takes place under mild temperatures (80-100°C). Exposure to other wavelengths, or absence of light failed to provide activity thus proving the plasmonic effect. Compared to other catalytic systems, the plasmonically activated catalyst provides access to primary and secondary alcohols using milder conditions, in a highly atom economical fashion. We showed that this reaction happens with perfect selectivity for C=O over C=C double bonds. Plasmonic catalysis of the oxidation of aldehyde to carboxylic acid was also demonstrated.



COLL 425

Synthesizing cooperative metal-support interfaces for catalysis

Sheng Dai^{2,1}, dais@ornl.gov. (1) Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States (2) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

Understanding the cooperative interactions of metals with active supports is essential to tailoring their catalytic activities and/or control of reaction pathways. These interfacial interactions can be achieved through two mechanisms: (1) interfacial charge redistribution (electronic interaction) and (2) interfacial atom transport (chemical interaction). In the last few years, a number of methodologies have been made by our research team toward tuning the metal-support interactions. The success of our approach capitalizes on nanoconfined spaces (e.g., confined interface restructuring), complex oxide supports (e.g., perovskite oxides), and 2D material edge sites (e.g., boron nitride), demonstrating that uniquely strong interfacial interactions and cooperativities between nanoparticles and supports can emerge through judicious structural choices of metals and supports. Our presentation will focus on the following three synergistically linked research activities: (1) sacrificial strong metal-support interactions, (2) “intelligent” metal-support interactions, and (3) charge-flow metal-support interactions. The interconnections among the above three metal-support interactions will be also discussed.

COLL 426

Chemical transformations in mesoporous transition metal oxides

Steven L. Suib, steven.suib@uconn.edu. Univ of Connecticut, Storrs Mansfield, Connecticut, United States

This presentation will focus on chemical transformations in mesoporous transition metal oxides prepared by inverse micelle syntheses. Besides initial nucleation and formation of pores, these systems go through a number of chemical transformations as well as after these stages. Various conditions can be used to control pore sizes, crystallinity, and phases. In addition, chemical transformations can occur such as generation of sulfides from oxides, and doping of these systems. Besides discussion of syntheses, we will discuss characterization and potential applications such as adsorption, catalysis, batteries, and others.

COLL 427

Single-facet dominant anatase TiO₂ (101) and (001) model catalysts to elucidate the active sites for alkanol dehydration

Yuan Chen¹, Lu Zhang¹, Huamin Wang¹, Donghai Mei¹, Libor Kovarik¹, Feng Gao¹, Berlin Sudduth², Enrique Iglesia³, **Yong Wang**^{1,2}, yong.wang@pnnl.gov. (1) Pacific Northwest National Laboratory, Richland, Washington, United States (2) Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington, United States (3) Univ of California at Berkeley, Berkeley, California, United States

Two anatase titania model catalysts, with preferential exposure of (101) and (001) facets, were synthesized and studied for 2-propanol dehydration. A series of microscopic and spectroscopic techniques including XRD, SEM/TEM, NH₃-TPD, DRIFTS and chemical titration were employed to correlate the structure properties of the model catalysts to their catalytic performances. Based on selective site poisoning titration using 2,6-di-tert-butyl pyridine, surface Lewis acid sites were found to be active for 2-propanol dehydration. The higher activity for TiO₂ (101) catalyst was ascribed to its higher acid strength and density in comparison to TiO₂ (001). Temperature-dependent DRIFTS were used to describe possible surface species under steady-state reaction conditions. Based on which, model surface structures were constructed on which 2-propanol dehydration was simulated with density functional theory. In both cases, 2-propanol was found to dehydrate via concerted E2 elimination pathways, but with different extents of surface O (or OH) participation. The results reported here clearly reveal faceting effects of metal oxides for alcohol dehydration and shed lights on catalytic oxygen removal for biomass-derived chemicals on metal oxide catalysts in general.

COLL 428

Reactivity of a heterostructured plasmonic biomaterial: Gold nanoparticles on ferritin

Daniel R. Strongin, dstrongi@temple.edu, Elizabeth B. Cerkez, Yonatan Ghidey, Alexandra Bruefach, Farbod Alimohammadi, Ann Valentine. Department of Chemistry, Temple University, Philadelphia, Pennsylvania, United States

The photochemistry of a plasmonic biomaterial that consisted of gold nanoparticles (AuNP) on the exterior of the iron sequestration protein, ferritin (Ftn), was investigated. The light driven photochemistry of the hybrid system was investigated mechanistically and for the reduction of chromate, Cr(VI) as CrO₄²⁻. In the absence of aqueous Cr(VI), the Fe(III) oxyhydroxide semiconducting core of Ftn underwent, in part, photoreactions to release Fe(II) when exposed to light with wavelengths, λ , < 475 nm. AuNP grown on the exterior of the Ftn produced plasmonic heterostructures (Au/Ftn) that allowed similar photochemistry to occur at longer wavelengths of light (i.e., λ > 475 nm). We also showed that Au/Ftn facilitated the reduction of Cr(VI) to Cr(III) in the presence of visible light (λ > 475 nm), while similar chemistry was not observed for Ftn (in the absence of Au) in the same spectral region. Overall, the presence of AuNP on the exterior of Ftn extended the photochemistry of Ftn for Fe(II) release and Cr(VI) reduction to longer wavelengths of light relative to Au-free Ftn. Results from spectroscopic techniques will

be presented that help understand the mechanism by which AuNP affect the photochemistry of Au/Ftn.

COLL 429

Engineering the nano-bio interface for nanomedicine applications

Kimberly Hamad-Schifferli, kim.hamad@umb.edu. Engineering, University of Massachusetts Boston, Boston, Massachusetts, United States

The convergence of the fields of nanotechnology and medicine has resulted in innovative approaches for novel disease therapies, biomedical imaging and sensing, and numerous others. In particular, the use of gold nanoparticles in rapid diagnostics for infectious diseases has been emerging as an application with the potential to address some of the major challenges in global health. These assays are low-cost and can be used in rugged environments, so they are attractive for widespread deployment for disease surveillance, quarantining, and treatment. One of the biggest challenges for effectively using nanoparticles in biological applications is the physical interface between the nanoparticles and its biological environment. Surface fouling and non-specific adsorption can lead to undesirable side effects such as diminished targeting specificity and cell uptake, unfavorable biodistribution, and toxicity. However, non-specific adsorption can actually be exploited for biological applications. We show how the unique properties of protein coronas and the nano-bio interface in general can be utilized for different medical applications including disease diagnostics for dengue, zika, chikungunya, Ebola, and other pathogens. We will discuss the unique interface issues in lateral flow immunoassays, and also discuss how multicolored nanoparticles can important new capabilities to the assays.

COLL 430

Assessment of nanoparticles disruption to quantify drug delivery *in vitro*

Eugenia Nogueira, Ana Loureiro, Artur Cavaco-Paulo, artur@deb.uminho.pt. University of Minho, Braga, Portugal

Efficient nanoparticle disruption inside the cells is a key for success with any type of drug delivery system. The efficacy of drug delivery is currently evaluated by direct visualization of labeled liposomes internalized by cells, not addressing objectively the release and distribution of the drug. Here, we propose a novel method to easily assess particle disruption and drug release into the cytoplasm. We propose the encapsulation of the cationic dye to detect an increase in fluorescence due to its specific binding to negatively charged DNA. For that, the dye needs to be released inside the cell and translocated to the nucleus. The present approach correlates the intensity of detected fluorescent dye with liposome disruption and consequently assesses drug delivery within the cells.

COLL 431

Development of target-specific 2A3 antibody-conjugated gold nanoclusters for assessment of cancer progression and inhibition of cancer cell proliferation

Jui Chi Kuo¹, b812105002@tmu.edu.tw, Shih-Hua Tan¹, Xi-Yu Pan², Kuan Chen¹, Ting-Kuang Chang¹, Tsung-Rong Kuo². (1) School of Biomedical Engineering, College of Biomedical Engineering, Taipei Medical University, Taipei, Taiwan (2) Graduate Institute of Nanomedicine and Medical Engineering, College of Biomedical Engineering, Taipei Medical University, New Taipei city, Taiwan

Fluorescent gold nanoclusters conjugated with 2A3 antibody (2A3-AuNCs) were developed for assessment of cancer progression and inhibition of cancer cell proliferation. The 2A3 antibody can specifically bind onto carcinoembryonic antigen-related cell adhesion molecule 6 (CEACAM6) on the cancer cell surface to decrease cancer cell proliferation, metastasis and angiogenesis. In this work, the target-specific 2A3-AuNCs were applied as the fluorescent probes to target CEACAM6 overexpressed pancreatic cancer. After binding with CEACAM6, the fluorescence changes of 2A3-AuNCs were measured and calculated to simulate their kinetics for assessment of pancreatic cancer progression by time-lapse confocal fluorescence microscopy. Moreover, the fluorescence imaging and fluorescence change of 2A3-AuNCs were applied to investigate their possibility for inhibition of pancreatic cancer cell proliferation. Eventually, we hope that we will be able to develop a practical application of target-specific AuNCs as a fluorescent probe for assessment of cancer progression and inhibition of cancer cell proliferation.

COLL 432

Soysome: A new class of self-assembled colloid from soybean oil fatty acids for nanoscale drug delivery applications

Mohiuddin A. Quadir, mohiuddin.quadir@ndsu.edu, Ruvimbo Chitemere, Dean C. Webster. Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States

A new class of biobased colloid—Soysomes—have been discovered and investigated. These colloids are obtained from sucrose soyate polyols, which are derived from esterification of soybean oil fatty acids and sucrose. We observed for the first time that, when MSSP is nanoprecipitated from organic solvent to water, they form uniformly distributed colloidal nanoparticles within the size range of 50-150 nm. Size of these nanoparticles are tightly controlled, and depends on the fabrication conditions and solvent-couples used. Interestingly, without the aid of poly(ethylene glycol) or of any surfactants, these soysomes were found to be stable in water for an extended period of time (> 6 months) and can withstand the destabilizing effect of temperature and pH. Soysomes are biocompatible, and are able encapsulate and transport hydrophobic drug molecules, and can be conjugated with hydrophilic active agents. We have investigated

and will report the synthesis and structure-function relationship of these new class of colloidal materials, basic physico-chemical and material properties, drug loading and release capacity, as well as their engagement with mammalian cells.

COLL 433

Structural remodeling of high-density lipoproteins in patients with diabetes mellitus

Clive L. Baveghems, *baveghem@bu.edu*, *Shobini Jayaraman*, *Olga Gursky*. *Physiology and Biophysics, Boston University School of Medicine, Boston, Massachusetts, United States*

Dysregulation of lipid metabolism is implicated in diabetes mellitus and cardiovascular disease. High-density lipoproteins (HDL), which remove excess cholesterol from cells, form a heterogeneous population of mature spherical and nascent discoidal particles 8-12 nm in diameter. Mature HDL contains a core of apolar lipids (cholesterol esters, triacylglycerol) and a surface of polar lipids (phospholipids, cholesterol) stabilized by apolipoproteins, mainly apoA-I and apoA-II. ApoA-I provides a structural scaffold and a functional ligand on the particle surface, and apoA-II modulates HDL structure-function and stability. We have probed the structural and compositional changes in HDL upon the onset of diabetes. Our goal is to test a hypothesis that increased triglyceride content decreases structural stability of plasma HDL. Blood samples were collected from cohorts of patients who were normolipidemic and normoglycemic (NL-HDL), diabetic with good glycemic control due to medication (GC-HDL), and newly diagnosed diabetic with poor glycemic control (PC-HDL). Lipoproteins were studied for biochemical composition, structure and stability by using circular dichroism spectroscopy, SDS, native gel electrophoresis, Western blotting, and negative staining electron microscopy. MALDI-TOF mass spectrometry shows the absence of post-translational modifications in all major apolipoproteins. Irrespective of the cohort, there is an inverse correlation between increased triglyceride content and lipoprotein stability. However, changes in HDL triglycerides associated with diabetes are not large enough to affect HDL stability. The results also suggest an increased degradation rate of HDL proteins in the PC-HDL group when compared to GC-HDL or NL-HDL, which is currently under investigation.

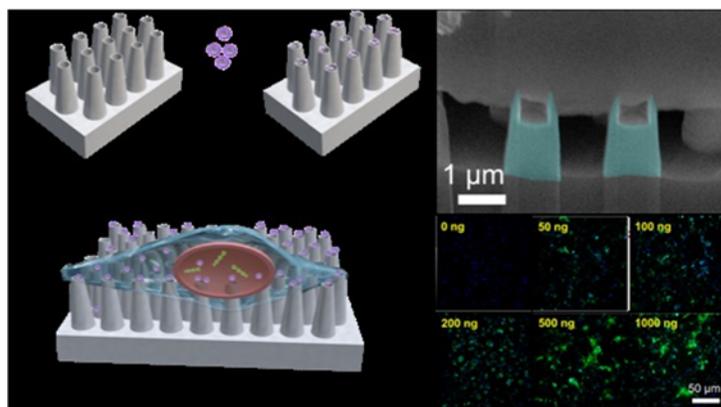
COLL 434

Silicon nanostructures for high-throughput intracellular gene delivery

Chuanzhen Zhao¹, *chuanzhenzhao@gmail.com*, *Qing Yang*¹, *Shuang Hou*^{2,3}, *Xiaobin Xu*^{1,4}, *Natcha Wattanatorn*¹, *Wenfei Liu*¹, *Hsian-Rong Tseng*^{2,3}, *Steven J. Jonas*^{2,5}, *Paul S. Weiss*^{1,6}. (1) *California NanoSystems Institute, Department of Chemistry & Biochemistry, UCLA, Los Angeles, California, United States* (2) *California NanoSystems Institute, UCLA, Los Angeles, California, United States* (3) *Department of Molecular and Medical Pharmacology, UCLA, Los Angeles, California, United States* (4) *School of Materials Science and Engineering, Nanyang Technological University, Los Angeles,*

California, United States (5) Department of Pediatrics, David Geffen School of Medicine, Eli & Edythe Broad Center of Regenerative Medicine and Stem Cell Research, Children's Discovery and Innovation Institute, UCLA, Los Angeles, California, United States (6) Department of Materials Science and Engineering, UCLA, Los Angeles, California, United States

High-throughput intracellular delivery is at the heart of numerous biomedical applications, including the delivery of membrane-impermeable drugs, gene editing, and regenerative medicine. Conventional viral-based strategies suffer from concerns over safety, cell viability, and high costs that have impeded their adoption. Non-viral strategies, such as cell membrane disruption-mediated approaches, have emerged as promising platforms. Direct, physical penetration of cell membranes using sharp nanostructures has been explored as a less destructive method. Here, we fabricate silicon nanovolcanos (SNVs) arrays for delivery of biomolecular cargos with high efficiency while maintaining high cell viability. Using multiple-patterning nanosphere lithography (MP-NSL), SNV structures were prepared with fully tunable geometric parameters (pitch, height, rim diameter, and hole depth), possessing hollow, syringe-like points at the apex, and less than 20 nm wall thickness. The sharp tips of SNVs enable penetration of cell membranes while minimizing disruption of cell functions. Biomolecular payloads loaded into the SNV cavities are delivered inside the cell upon penetration. We demonstrate successful delivery of membrane-impermeable enhanced green fluorescent protein plasmids with 80% transfection efficiency and near 90% cell viability after delivery of nucleic acids. With these advances in high transfection efficiency and viability, SNVs provide a versatile platform for a wide range of fundamental and clinical applications.



COLL 435

Coacervation-based model systems for intracellular compartmentalization

Allyson Marianelli¹, allyson.m.marianelli@gmail.com, **Brian Miller**¹, **Miah Sherman**², **Christine D. Keating**¹. (1) Chemistry, Pennsylvania State University, University Park, Pennsylvania, United States (2) Biochemistry and Molecular Biology, Pennsylvania State University, University Park, Pennsylvania, United States

Experimental model systems for living cells provide a route to study the physicochemical behavior of the cell while eliminating some of the inherent biocomplexity. A number of membraneless organelles that exhibit liquid-like behavior (e.g. nucleoli, P granules, and Cajal bodies) have recently been discovered, making coacervation of biopolymers into a dense polymer-rich liquid phase an attractive model for these organelles. However, coacervation alone does not capture key aspects of the intracellular environment. The cellular milieu contains a wide variety of macromolecules that combine to make up ~30 wt.% of the cell, leading to a macromolecularly crowded solution. Crowding can significantly impact biomolecular structures and interactions, making it an important consideration in experimental model systems. Investigation of coacervation in the presence of varying crowders and their small molecule analogues provides insight into the ways in which the crowded intracellular environment may impact liquid-liquid phase separation (LLPS). The numerous membraneless organelles that exist within cells each have unique biopolymer content and function, and may form via different LLPS mechanisms. These membraneless compartments are utilized alongside membrane-bound organelles to localize and modulate bioactivity. The combination of coacervation, both simple and complex, with neutral polymer aqueous phase separation mimics the variety of liquid microcompartments that can exist in living cells. Encapsulation of coacervate systems within membrane-bound vesicles provides additional complexity to the cellular mimic. This work makes coacervation-based model systems for intracellular organization more accurate through the incorporation of macromolecular crowding, neutral polymer aqueous phase separation, and membrane-bound compartments.

COLL 436

Gold nanoparticles as radiosensitizers demonstrated in a chick chorioallantoic membrane model

Carly S. Filgueira¹, *carly.levin@gmail.com*, **Francesca Ferraro**¹, **Veronica Vighetto**¹, **Nicola DiMarzio**¹, **Ravi Pathak**³, **Hsuan-Chen Liu**³, **Arvind Pandey**⁴, **Mariana Villanueva**³, **Corrine Ying Xuan Chua**¹, **Sankar Mitra**⁴, **Andrew Sikora**³, **Naomi J. Halas**², **Alessandro Grattoni**¹. (1) *Nanomedicine, Houston Methodist Research Institute, Houston, Texas, United States* (2) *Rice Univ Ece Dept, Houston, Texas, United States* (3) *Head and Neck Cancer Program, Baylor College of Medicine, Houston, Texas, United States* (4) *Radiation Oncology, Houston Methodist Research Institute, Houston, Texas, United States*

At diagnosis, most patients with non-small cell lung cancer (NSCLC) have non-resectable tumors or cannot withstand surgery; creating a need for treatment alternatives. Radiotherapy has become one of the primary tools to treat and prevent the spread of abnormal cancerous cells and is used to treat a variety of cancer types. Radiotherapy can be used on its own, after surgery, or concurrent or after chemotherapy, as high energy radiation shrinks tumors and kills cancer cells. Gold nanoparticles (Au nps) are efficient sensitizers for radiation therapy. When incorporated into tumor tissue and irradiated, Au nps specifically enhance the radiation effects up to

200%. This leads to a higher dose of X-rays to the cancerous tissue as compared with normal tissue during a radiotherapy treatment. Au nps have been demonstrated to be effective radiosensitizers in solid tumors with an effect directly on DNA damage as well as a release of tumor antigens. Importantly, the radioenhancing effect of Au nps can be exploited for triggering a systemic immunological response to distributed metastases through the abscopal effect, which has been observed clinically as a result of radiotherapy. We propose to test the theory that enhanced radiotherapy through delivery of Au nps can produce an anti-tumor response for lung cancer treatment. Intratumoral injection of Au nps combined with X-ray radiation as therapy for Lewis Lung carcinoma is presented for C57BL/6 mice inoculated with cells expressing luciferase (LLC-Luc). In this work, results are also presented for the chick chorioallantoic membrane (CAM) as a tumor model. This study showed that the CAM can be used as preliminary *in vivo* model to study the effects of different treatments, using a simpler and faster system in which the influence of the immune system is not present and which does not require the IACUC approvals.

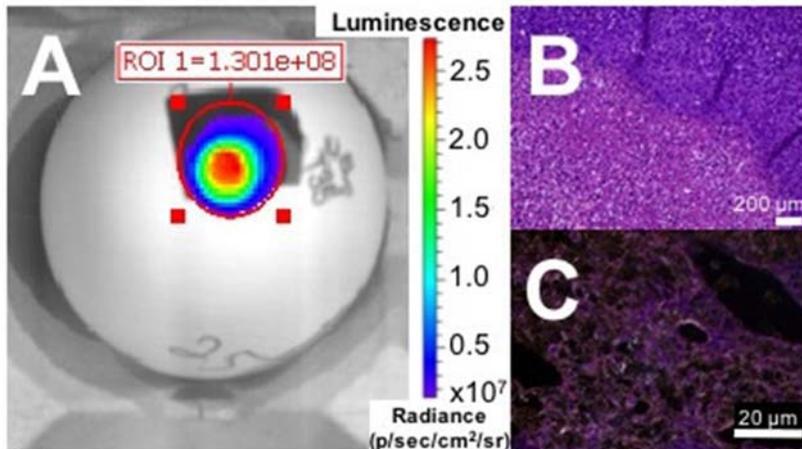


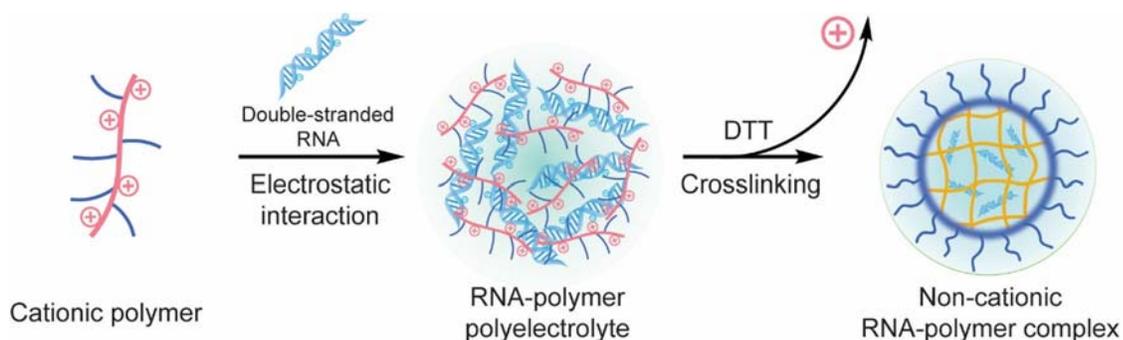
Figure 1. Example of (A) a luciferase expressing Lewis Lung tumor grown *in ovo* imaged using an In Vivo Imaging System where the bioluminescence signal is marked by the region of interest. (B) H&E and (C) silver stain assessment of the tumor *in ovo*.

COLL 437

Non-cationic RNA-polymer complexes for RNA interference

Ziwen Jiang¹, jiangziwen@live.cn, **Wei Cui**², **Jesse Mager**², **Sankaran Thayumanavan**³. (1) Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Department of Veterinary and Animal Sciences, University of Massachusetts Amherst, Amherst, Massachusetts, United States (3) Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, United States

RNA interference (RNAi) requires the intracellular delivery of RNA molecules to initiate the neutralization of targeted mRNA molecules, inhibiting the expression or translation of the targeted gene. Current polymers and lipids that are used to deliver RNA molecules are generally required to be positively charged, to achieve complexation with RNA and the cellular internalization. However, cationic surface charge has been implicated as the reason for toxicity in many of these systems. Herein, we report a novel strategy to generate non-cationic RNA-polymer complexes for RNA delivery with significantly reduced cytotoxicity. We use an in situ electrostatic complexation using a methylated pyridinium group, which is removed during the RNA binding step. The resultant complexes demonstrate successful knockdown in preimplantation mammalian embryos, providing a new approach for nucleic acid delivery.



COLL 438

Scalable fabrication of one- and two-dimensional gold nanostructures for plasmonic biosensing applications

Chuanzhen Zhao¹, chuanzhenzhao@gmail.com, Xiaobin Xu^{1,2}, Abdul R. Ferhan², Naihao Chiang^{1,2}, Joshua A. Jackman², Qing Yang¹, Wenfei Liu¹, Anne M. Andrews^{3,4}, Nam-Joon Cho², Paul S. Weiss^{1,5}. (1) California NanoSystems Institute, Department of Chemistry & Biochemistry, UCLA, Los Angeles, California, United States (2) School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore (3) California NanoSystems Institute, UCLA, Los Angeles, California, United States (4) Department of Psychiatry and Biobehavioral Health, Semel Institute for Neuroscience and Human Behavior, and Hatos Center for Neuroparmacology, UCLA, Los Angeles, California, United States (5) Department of Materials Science and Engineering, UCLA, Los Angeles, California, United States

Plasmonic nanostructures made from noble metals have broad application in chemical and biological sensors, food safety, environmental monitoring, and biomedical devices. Scalable techniques to fabricate these structures with dimensions smaller than the wavelengths of visible light are critical to enable their widespread use. In this work, we demonstrate a large-area, high-throughput process to fabricate one-dimensional nanolines and two-dimensional square nanodisks with sub-micron dimensions for use as plasmonic biosensors. Commercially available HD-DVDs were employed as low-cost, large-area “masters” to prepare polymeric stamps with linear features 200 nm wide

at a pitch of 400 nm. This pattern was transferred onto gold films via chemical lift-off lithography and selective wet etching, thereby producing large-area arrays of plasmonic Au nanolines. Repeating the patterning process with stamps rotated 90° from the initial patterning orientation enabled the conversion of 1D nanolines to 2D arrays of nanodisks. By tracking peak shifts in the extinction spectra of these plasmonic nanostructures, it was possible to conduct transmission-mode refractometric sensing experiments in aqueous environments, and the corresponding bulk refractive index sensitivities were determined to be in the range of 200–500 nm/refractive index units. These sensing capabilities were translated into high-sensitivity detection of the interactions between these plasmonic nanostructures and different classes of biomacromolecules, namely zwitterionic lipid vesicles and bovine serum albumin protein. Taken together, the results demonstrate how this scalable patterning technique provides a simple and economical means to produce large-area plasmonic nanostructures for a variety of applications in optoelectronics and biosensing.

COLL 439

Nano-scale interfacial reversible protein folding of amyloidogenic peptides

Kazushige Yokoyama, yokoyama@geneseo.edu. *Chemistry, The State University of New York Geneseo College, Rochester, New York, United States*

This research focuses on a folding or unfolding process of amyloidogenic peptides, amyloid beta, alpha synuclein and beta-2 microglobulin under an interfacial environment. We use an approach to provide surface potential required for a folding through nanogold colloidal particles. The folded or unfolded conformation of peptides can be prepared by externally changing the pH to pH10 or pH4, respectively. Corresponding the folded or unfolded conformation of the peptides pre-adsorbed over the gold particles create either dispersed or aggregated condition of gold particles, resulting in a no-shift or red-shift of SPR (Surface Plasmon Resonance) band for various sizes of gold colloids. Generally speaking, the enhancement of the reversible self-assembly depend on the size of nano-gold colloid. The temperature- dependence of the reversibility exhibited a complex feature. Mostly, the enhancement took place at the relatively higher temperature. However, the opposite trends were observed depending on the peptide studied.

COLL 440

Colloidal nanocrystals of APbX₃ perovskites [A=Cs⁺, CH(NH₂)₂²⁺, X=Cl⁻, Br⁻, I⁻]: Surface chemistry, self-assembly and potential applications

Maksym Kovalenko^{1,2}, mvkovalenko@ethz.ch. (1) *Lab Inorganic Chem, HCI H 123, ETH Zurich, Zurich, Switzerland* (2) *Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Zurich, Switzerland*

Here, we survey the synthesis method for colloidal lead halide perovskite nanocrystals (APbX₃, NCs, A=Cs⁺, FA⁺, FA=formamidinium; X=Cl, Br, I) and prospects of these NCs for optoelectronic applications such as in television displays, light-emitting devices, and solar cells, emphasizing the practical hurdles that remain to be overcome. The spontaneous and stimulated emission spectra of these NCs are readily tunable over the entire visible spectral region of 410-700 nm. The photoluminescence of these NCs is characterized by narrow emission line-widths of 12-42 nm, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 100%. Cs_{1-x}FA_xPbI₃ and FAPbI₃ reach the near-infrared wavelengths of 800 nm. Their processing and optoelectronic applications are, however, hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface capping molecules during isolation and purification. To address this issue, we have developed a new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules such as 3-(N,N-dimethyloctadecylammonio) propanesulfonate, resulting in much improved chemical durability. In particular, this class of ligands allows for the isolation of clean NCs with high photoluminescence quantum yields of above 90% after 4 rounds of precipitation/redispersion along with much higher overall reaction yields of uniform and colloidal dispersible NCs. Densely packed films of these NCs exhibit high photoconductivity, high photoluminescence quantum yields and low thresholds for amplified spontaneous emission. Perovskite NCs also readily form long-range ordered assemblies known as superlattices. These assemblies exhibit accelerated coherent emission (superfluorescence), not observed before in semiconductor nanocrystal superlattices.

COLL 441

Utility of PEGylated dithiolane ligands for controlled synthesis of water-soluble metal nanocrystals

Eunkeu Oh^{1,2}, eunkeu.oh.ctr.ks@nrl.navy.mil, Kimihiro Susumu^{1,2}, Christopher Klug¹, James Delehanty¹, Alan Huston¹, Igor Medintz¹. (1) US Naval Research Laboratory, Washington, District of Columbia, United States (2) KeyW Corp, Hanover, Maryland, United States

Metallic nanoparticles or nanocrystals are being developed for a variety of applications including catalysis, drug delivery and contrast agents for high-resolution imaging. We have demonstrated the general utility of PEGylated dithiolane ligands for direct synthesis of high quality water-soluble Au, Ag, Pt, Pd, Cu and alloyed/bi-metallic nanoparticles. The PEGylated ligands with different terminal groups can be used to allow for the bio-functionalization of Quantum dots, magnetic nanoparticles, and many other types of core/shell nanoparticles. Additionally these ligands are suitable for use with a variety of different reducing methods that control the shape and size of nanoparticles. The prepared nanoparticles exhibit remarkable stability in various chemical environments and the controlled functionalization of the surface expands the potential areas of application.

COLL 442

Continuous flow synthesis of semiconductor nanoparticles using a modular millifluidic platform

Ajit Vikram¹, vikram2@illinois.edu, Vivek Kumar¹, Utkarsh Ramesh¹, Karthik Balakrishnan¹, Nuri Oh², Kishori Deshpande⁴, Trevor Ewers⁵, Peter Trefonas⁶, Moonsub Shim², Paul J. Kenis³. (1) Chemical & Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Material Science and Engineering, University of Illinois, Urbana, Illinois, United States (3) Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Champaign, Illinois, United States (4) Dow Chemical Company, Lake Jackson, Texas, United States (5) Dow Chemical Company, Midland, Michigan, United States (6) Dow Electronic Materials, Marlborough, Massachusetts, United States

Emerging nanostructures of colloidal quantum dots (QD) provide the potential to tune the optoelectronic properties by varying shape, size, and morphology, which in turn makes them viable material for applications ranging from cellular imaging to display technology. Despite significant progress in synthetic route, the reproducible synthesis of high quality heavy-metal free QDs still remain a challenge. Most of the reported work in the field has focused on QD synthesis using small-scale conventional batch reactors, that are limited by poor control over reaction conditions in terms of heating/cooling/mixing of the precursors. Recent advancements in continuous flow synthesis using microfluidic platforms has shown promise to subdue the challenges of batch synthesis. However, synthesis of heavy-metal free QDs exhibiting high photoluminescence quantum yield (QY) at high production rates, are yet to be achieved using continuous flow platforms.

This presentation will focus on design and application of a simple yet robust millifluidic continuous flow reactor setup for synthesis of heavy-metal free semiconductor nanoparticles. The modular continuous flow platform allowed the synthesis of InP/ZnSeS core-shell quantum dots exhibiting QY as high as 67% with good reproducibility (< 5% std. dev.), while maintaining high productions rates (100-200 mg/hour using a single-channeled reactor). By varying the process parameters (flow rates, temperature and concentration) at different stages, the emission wavelength of InP/ZnSeS nanoparticles can be tuned to span nearly the entire visible spectra (blue-red). The continuous flow setup also allows real-time product analysis using inline absorbance/photoluminescence flow cells, enabling rapid screening of different reaction parameters. Due to precise control of reaction conditions, the modular platform can also be applied for synthesis of a wide range of nanostructures ranging from quantum dots to nanorods to even more complex nanostructures, with enhanced control over shape, size, and morphology.

COLL 443

Synthesis of alloy nanoparticles via sputtering onto a liquid polymer

Mai T. Nguyen, *mai_nt@eng.hokudai.ac.jp*, Tetsu Yonezawa, Lianlian Deng. Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido, Japan

Bimetallic alloy nanoparticles are attractive for their tunable, new, and synergistic properties. Thus a synthesis method for bimetallic alloy nanoparticles with desired structures, compositions, and sizes is in demand. Recently, vacuum sputtering onto a liquid has been emerging as a green approach to create bimetallic nanoparticles dispersed in liquid. Vacuum sputtering generate atoms/clusters from bulk metal targets which subsequently experience collision and growth to form nanoparticles in gas, gas-liquid interface and liquid inserted in sputtered chamber. The liquids are low volatile and can be used to capture the formed nanoparticles. It is versatile to choose the liquids and their functionalities to stabilize nanoparticles and to control particle size. In our study, double target sputtering has been developed to create alloy nanoparticles with tailorable composition via simultaneously sputtering two metal targets and varying sputter currents used for each target. We have chosen liquid polyethylene glycol, PEG, M. W. = 600, as the liquid substrate for stabilizing the sputtered particles. Our research focuses on investigating the possibility of bimetallic solid solution nanoparticles formed at room temperature via double target sputtering of different metal systems. Two metals used including complete miscible, intermetallic compounds, and immiscible systems in the bulk state, i.e. Au/Ag, Au/Cu, and Au/Pt respectively. Our results indicated that the solid solution alloy nanoparticles were produced in each system. In particular, the positions of localized surface plasmon resonance peak positions of Au/Ag nanoparticles were linearly dependent on the compositions of the sputtered nanoparticles, which suggested the alloy formation. Besides, elemental mapping images of the obtained Au/Ag nanoparticles (using a transmission electron microscope (TEM)-energy dispersive X-ray spectroscopy (EDX)) exhibited a uniform distribution of two metals for entire nanoparticles. This further confirmed the formation of bimetallic alloy. Similar results were obtained for Au/Cu and Au/Pt nanoparticles despite the fact that they are not solid solution in the bulk state. Hence, our method is promising for synthesis of various alloy nanoparticles with controllable composition, size, and good colloidal stability.

COLL 444

Graphene inks as versatile templates for printing tiled metal oxide crystalline films

Muchun Liu^{1,2}, *muchun_liu@brown.edu*, Robert Hurt². (1) Chemistry, Brown University, Providence, Rhode Island, United States (2) Dept of Engineering, Brown Univ, Providence, Rhode Island, United States

There is great interest in exploiting van der Waals gaps in layered materials as confinement reaction vessels to template the synthesis of new nanosheet structures. The gallery spaces in multilayer graphene oxide, for example, can intercalate hydrated metal ions that assemble into metal oxide films during thermal oxidation of the sacrificial graphene template. This approach offers limited control of structure, however, and does not typically lead to 2D atomic-scale growth of anisotropic platelet crystals, but rather

arrays of simple particles directionally sintered into porous sheets. Here we demonstrate a new graphene-directed assembly route that yields fully-dense, space-filling films of tiled metal oxide platelet crystals with tessellated structures. The method relies on colloidal engineering to produce a printable “metallized graphene ink” with accurate control in metal loading, grain size/porosity, composition and micro/nano-morphologies, and is capable to achieve higher metal-carbon ratio than is achievable by intercalation methods. These tiled structures are sufficiently robust to create free standing papers, complex microtextured films, 3D shapes, and metal oxide replicas of natural biotextures.

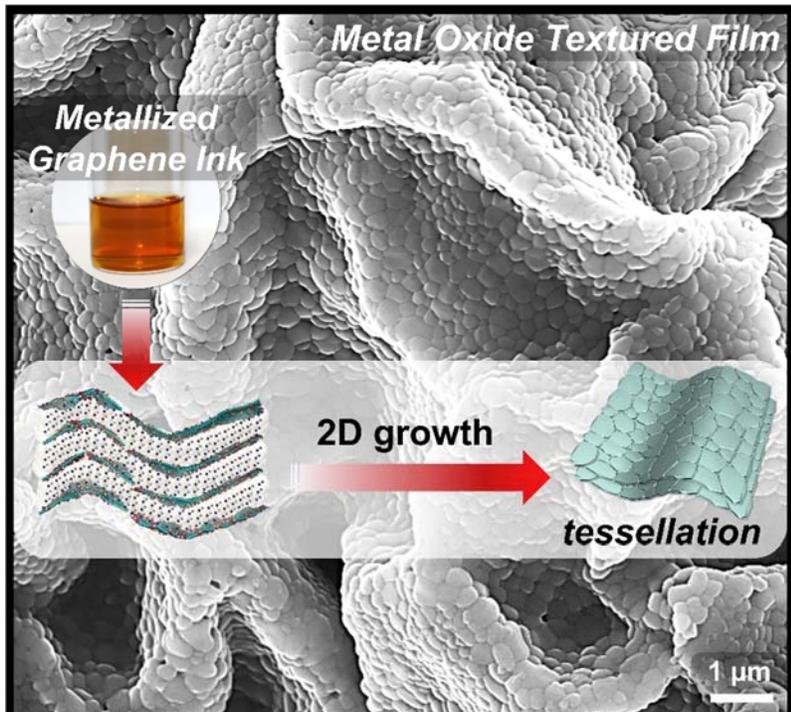
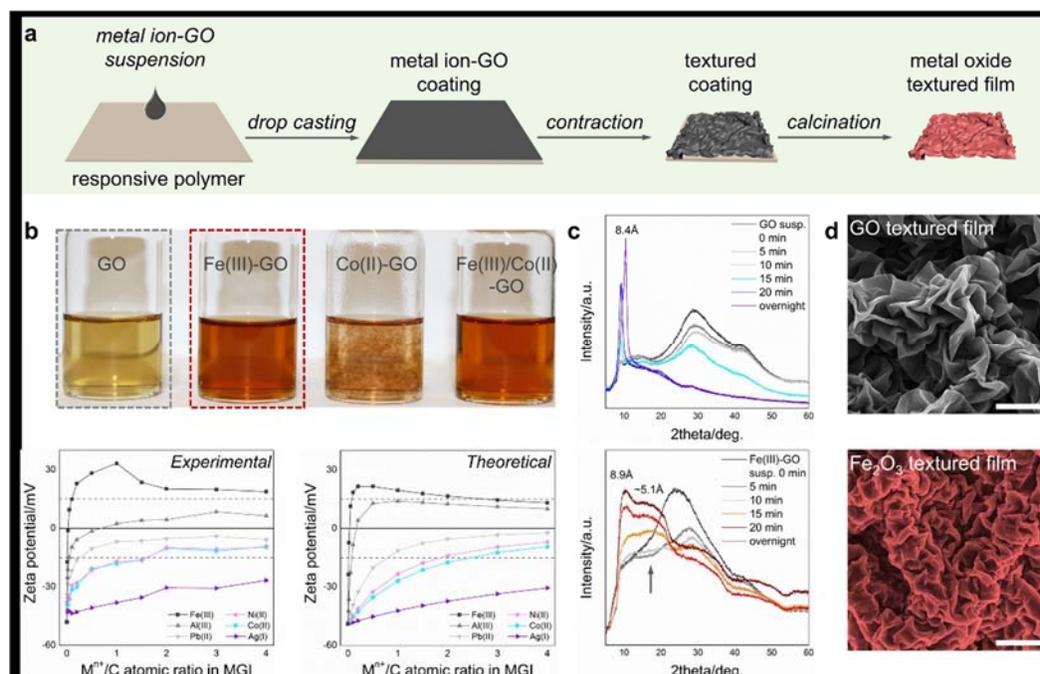


Table of contents



COLL 445

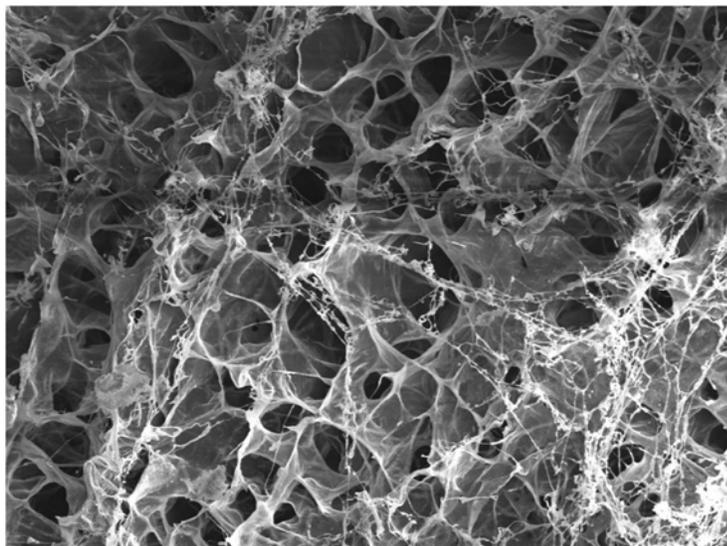
Highly functionalised water-soluble fullerene derivatives: Cage size affects hierarchical self-assembled structures

Ilija Rasovic, ilija.rasovic@materials.ox.ac.uk, Kyriakos Porfyraakis. Department of Materials, University of Oxford, Oxford, United Kingdom

The fullerenes are a unique carbon allotrope family that boast many desirable properties for therapeutic and diagnostic applications in nanomedicine, such as improved magnetic resonance imaging (MRI) contrast agents, photodynamic therapy (PDT) agents and enzyme inhibitors, for example. These highly hydrophobic cages, however, must be modified in order to enter the human body safely and effectively, and avoid rejection. One such method is exohedral functionalisation: the covalent attachment of water-solubilising groups to the fullerene cage.

PEGylation (the covalent attachment of polyethylene glycol (PEG) chains) is often used to functionalise nanoparticles with the aim of negating rejection by the body. Inspired by this, but looking to reduce the dominance of the long PEG chain, we functionalised fullerenes C₆₀, C₇₀, C₈₄ and C₉₀ with triethylene glycol based chains. We have comprehensively characterised the resultant molecular structures. Strikingly, depending on the size of the fullerene cage, these molecular building blocks self-assemble in aqueous solution to give complex hierarchical structures with macroporous architectures defined by a network of tubular fibrils. The mechanical properties of these hydrogels have been investigated using atomic force microscopy. Not only are these findings of interest to the study of the fundamentals of self-assembly processes, but the

resultant hydrogel structures hold great promise for the utility of fullerenes in the field of nanomedicine.



COLL 446

Noncovalently functionalized 2D materials template solution growth of ultranarrow gold nanorods along 1-nm-wide rows of functional headgroups

Ashlin G. Porter¹, porter60@purdue.edu, Tianhong Ouyang², Tyler R. Hayes³, Shane R. Russell¹, Shelley A. Claridge¹. (1) Chemistry, Purdue University, West Lafayette, Indiana, United States (3) Chemistry, Purdue University, Lafayette, Indiana, United States

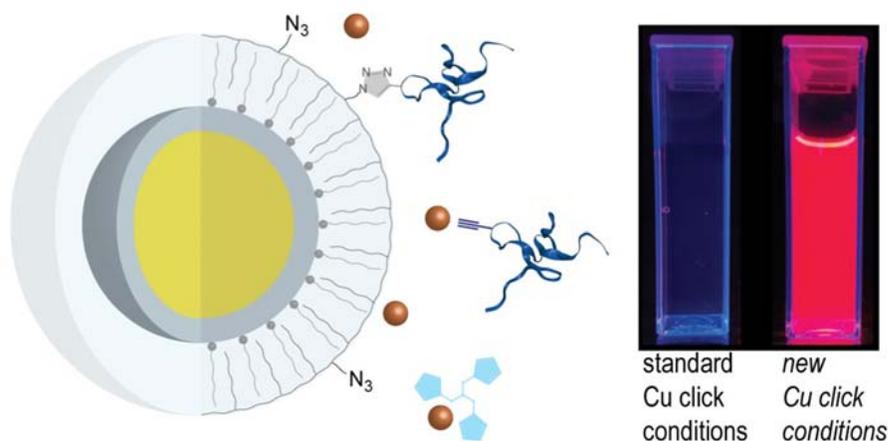
Layered material surfaces are commonly controlled by noncovalent monolayer chemistry. 2D materials frequently require robustness towards solvent and vacuum processing, as well as controlled interactions with their environment. Somewhat surprisingly, certain classes of monolayers can support these functions. We have demonstrated that 2D materials noncovalently functionalized with lying down phases of long chain amines including 4,6-pentacosadiynamine, 10,12-pentacosadiynamine and 23:2 diyne phosphoethanolamine can be photopolymerized and used as templates for the growth of gold nanowires. Wires synthesized in this manner have very controlled diameters of ~2 nm and lengths of 100-500 nm. All three monolayer templates result in differences in wire growth, due to the headgroup structure and range of motion, as well as chain architecture. These results suggest that noncovalently functionalized 2D materials may be useful templates to grow inorganic nanocrystals in a controlled fashion for plasmonically coupled arrays for nanoscale applications.

COLL 447

Azide-alkyne click conjugation on quantum dots by selective copper coordination

Victor Mann^{1,2}, victor.r.mann@gmail.com, **Alexander Powers**¹, **Drew Tilley**³, **Jon Sack**³, **Bruce E. Cohen**¹. (1) *The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States* (2) *Department of Chemistry, University of California, Berkeley, Berkeley, California, United States* (3) *Department of Physiology and Membrane Biology, University of California, Davis, Davis, California, United States*

Functionalization of nanocrystals is essential for their practical application, but synthesis on nanocrystal surfaces is limited by incompatibilities with certain key reagents. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) is among the most useful methods for ligating molecules to surfaces, but has been largely useless for semiconductor quantum dots (QDs) as Cu⁺ ions quickly and irreversibly quench QD fluorescence. To discover non-quenching synthetic conditions for Cu-catalyzed click reactions on QD surfaces, we developed a combinatorial fluorescence assay to screen >2000 reaction conditions to maximize cycloaddition efficiency while minimizing QD quenching. We identify conditions for complete coupling without significant quenching, which are compatible with common QD polymer surfaces and various azide/alkyne pairs. Based on insight from the combinatorial screen and mechanistic studies of Cu coordination and quenching, we find that superstoichiometric concentrations of Cu can promote full coupling if accompanied by ligands that selectively compete the Cu from the QD surface but allow it to remain catalytically active. Applied to the conjugation of a K⁺ channel-specific peptidyl toxin to CdSe/ZnS QDs, we synthesize unquenched QD conjugates and image their specific and voltage-dependent affinity for K⁺ channels in live cells.



COLL 448

New insights regarding the local atomic structure and magnetic properties in sub-10 nm iron oxide nanocrystals produced by a living growth process

Susan Cooper, susan.rudd.cooper@gmail.com, **Jim E. Hutchison**. *University of Oregon, Eugene, Oregon, United States*

Iron oxide nanocrystals have size-dependent structures and magnetic properties that are useful in a host of applications, ranging from water purification to biomedical applications. For example, very small nanocrystals have tetrahedrally coordinated iron vacancies on their surfaces that may enhance arsenite adsorption. They also have size- and structure- dependent magnetic properties. Despite these attractive properties, questions remain regarding the influence of size on local atomic structure and magnetic properties in small (< 10 nm diameter) iron oxide. Here we describe studies of a series of 13 distinct sizes of spinel iron oxide nanocrystals spanning a range of 4-9 nm, all synthesized under the same conditions using a new continuous growth synthesis. The only synthetic parameter that changes the size of the particles is the amount of precursor added: The solvent, surfactant and reaction temperature are the same for every size. As a consequence, these nanocrystals are nearly ideal for evaluating the size dependent properties and structure at this lengthscale. Magnetic measurements show that the saturation magnetization increases with size throughout the range. Further, the calculated magnetic size is essentially the same as the physical size, suggesting that nearly all the iron within the nanocrystal contributes to the magnetism. Detailed structural studies using Pair Distribution Function (PDF) analysis of total x-ray scattering measurements were carried out to probe the atomic-scale structure within these nanocrystals. These studies reveal size-dependent nanoscale structural features, including differences in tetrahedrally and octahedrally coordinated iron vacancies in the lattice.

COLL 449

Mitigating the off-target toxicity of nanomedicines through controlled release

Younan Xia, younan.xia@bme.gatech.edu. Molecular Science Engineering Building, Georgia Institute of Technology, Atlanta, Georgia, United States

We are developing a nanosystem to mitigate the off-target toxicity of an anticancer drug by precisely managing its instant concentration in healthy tissue *versus* tumor. Specifically, phase-change materials with a sharp melting point at 39 °C are formulated from natural fatty acids and further processed as uniform nanoparticles. The anticancer drug is directly loaded into the interior of the nanoparticles, in addition to the inclusion of a near-infrared dye for photothermal heating to quickly melt the solid matrix. For the nanoparticles accumulated inside the tumor, the drug is triggered to quickly release at a concentration above the lethal dose through the application of near-infrared irradiation. For those in healthy tissue, the drug is released very slowly at a safe dose as the carrier is naturally degraded. Additionally, the chemotherapy can be combined with photo-hypothermia to further improve the outcome while reducing the dosage of anticancer drug(s) involved. When optimized, this nanosystem promises to eradicate cancer cells in high efficacy, without involving the off-target toxicity and adverse impacts commonly associated with chemotherapy.

COLL 450

Nanoparticle-based approaches to drug delivery to peripheral nerve for pain and other conditions

Daniel S. Kohane, *daniel.kohane@childrens.harvard.edu*. *Anaesthesia, Boston Children's Hospital, Harvard Medical School, Newton, Massachusetts, United States*

A wide range of systems have been used to deliver drugs to peripheral nerve, usually to extend the duration of local anesthesia, i.e. to treat pain. Here we will discuss the role of nanoscience in this application, comparing it to the effects that can be achieved with non-nanoscale systems. Nanoscale systems can enable on-demand analgesia triggered by external energy sources, allowing patient control of the onset, intensity, and duration of local pain relief. The tissue depth at which local anesthetic effect can be triggered by external stimuli depends on many variables; a crucial one is the sensitivity of the delivery system to the stimulus. Nanoparticles of an appropriate size can penetrate directly into nerve, allowing delivery of drugs that would usually have difficulty getting in.

COLL 451

Kidney-targeting peptide amphiphile micelles toward renal drug delivery

Jonathan Wang, Eun Ji Chung, *eunchung@usc.edu*. *University of Southern California, Los Angeles, California, United States*

Molecular engineering of multifunctional, multivalent micelles provides a strategy for the detection and targeted delivery of therapeutics to many diseases including cardiovascular and chronic kidney disease. Moreover, the rational design of these nanoparticles has the potential to deliver signals to report back on or influence the regeneration of the cellular niche for personalized medicine regimes, while addressing the limitations of current diagnostic strategies. While small molecule drugs have been proposed as a therapy to manage kidney diseases, high dosages are often required to achieve therapeutic efficacy, generating off-target side effects, some of which are lethal. To address these limitations, a novel, kidney-targeting peptide amphiphile micelle (KPAM) system was designed toward drug delivery applications. Specifically, KPAMs were found to cross the glomerular filtration barrier and bind megalin, a multiligand cell surface receptor present on renal tubule cells. When incubated with human kidney proximal tubule cells, KPAMs were found to be biocompatible in vitro and showed higher accumulation in kidneys compared to nontargeted controls in vivo. We provide proof-of-concept studies for their utility in autosomal polycystic kidney disease and their application using various routes of administration.

COLL 452

Multifunctional zero- and one-dimensional nanomaterials for imaging, sensing and multidrug delivery

Anton Naumov^{1,2}, a.naumov@tcu.edu, **Md. Tanvir Hasan**¹, **Elizabeth Campbell**¹, **Roberto Gonzalez-Rodriguez**³, **Giridhar Akkaraju**⁴. (1) Physics and Astronomy, Texas Christian University, Fort Worth, Texas, United States (2) TCU and UNTHSC School of Medicine, Fort Worth, Texas, United States (4) Biology, Texas Christian University, Fort Worth, Texas, United States

The variability and adaptability of cancer types known to date can be better addressed with therapeutic strategies performing multiple functions: combination treatment simultaneously targeting several factors, molecular imaging tracing drug delivery pathways and biological sensing of cancer environments. We develop nanomaterials-based platforms for such multifunctional image-guided drug/gene therapies. Single-walled carbon nanotubes (SWCNTs) are used as one-dimensional carriers for anti-inflammatory siRNA and anti-fibrotic PX-866 drug delivery to liver intended to mitigate the effects of nonalcoholic steatohepatitis and prevent its potential translation into hepatocellular carcinoma. SWCNTs exhibit type-specific emission in the near-IR water window with reduced biological autofluorescence and high tissue penetration depth. In our work different SWCNT types are complexed to specific combination treatment drugs or genes to separately assess the therapeutic effect and the delivery pathways of each therapeutic.

Glucose-based quantum dots (GQDs) are developed in this work as an alternative zero-dimensional fully multifunctional platform providing dual color imaging and sensing of cancer environments. GQDs are specifically designed as biocompatible materials emitting fluorescence both in the visible (with up to 60% quantum yield) and near-infrared that can be potentially used for *in-vitro* and *in-vivo* detection respectively. pH-sensitivity of the emission allows for optical detection of cancer environments combining the essential optical diagnostic functions in one simplistic glucose-derived platform.

COLL 453

Intrinsically radiolabeled nanomaterials

Weibo Cai, wcai@uwhealth.org. University of Wisconsin, Madison, Wisconsin, United States

Radiolabeled nanomaterials have gained tremendous interest over the last 2 decades, which can play diverse roles in imaging, image-guided drug delivery, as well as theranostics of a number of diseases such as cancer. Although chelator-based radiolabeling techniques (commonly used for labeling nanomaterials with radiometals such as Cu-64/Zr-89) have been used for decades, concerns about the complexity of coordination chemistry, possible alteration of nanomaterial pharmacokinetics, and potential detachment of radioisotopes have driven the need for developing a simpler yet

better technique for future radiolabeling.

The emerging area of intrinsically radiolabeled nanomaterials can take advantage of the unique physical and chemical properties of well-selected inorganic or organic nanomaterials for radiolabeling, and more importantly, offer an easier, faster, and more specific radiolabeling possibility to facilitate future clinical translation. Generally speaking, the four major categories of intrinsically radiolabeled nanomaterials include: 1) hot-plus-cold precursors, 2) specific trapping, 3) cation exchange, and 4) proton beam activation.

Representative examples of each category will be briefly illustrated in this talk, with the main focus on our own recent work that involves the radiolabeling of a variety of nanomaterials via “specific trapping”. The nanomaterials investigated in our laboratory include iron oxide nanoparticles, micelles, silica-based nanoparticles, carbon-based nanomaterials, multifunctional/multimodal hybrid nanomaterials, among others.

COLL 454

Enhancing nanoparticle delivery to the tumor with a targeted agent and light

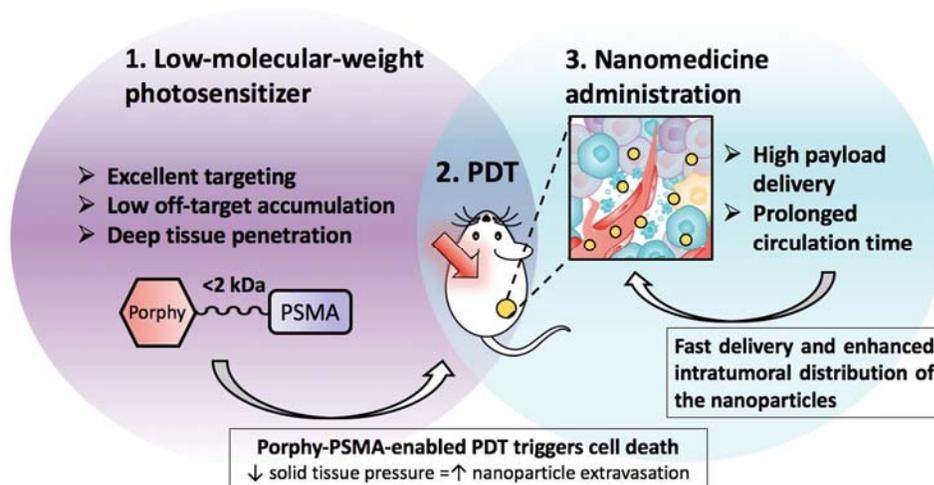
Marta Overchuk^{1,2}, marta.overchuk@gmail.com, Kara M. Harmatys², Shrey Sindhvani¹, Abdullah M. Syed¹, Juan Chen², Martin G. Pomper³, Warren Chan¹, Gang Zheng^{2,4}. (1) Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada (2) Princess Margaret Cancer Centre, University Health Network, Toronto, Ontario, Canada (3) The Russell H. Morgan Department of Radiology and Radiological Science, Johns Hopkins Medical Institutions, Baltimore, Maryland, United States (4) Medical Biophysics, University of Toronto, Toronto, Ontario, Canada

Drug encapsulation into a nanoparticle enables improved pharmacokinetics, decreased toxicity and co-delivery of multiple drugs with contrast agents. Despite being widely explored, this approach has not been proven more efficacious in cancer treatment compared to free chemotherapy drugs, primarily due to low nanoparticle tumor uptake and poor tissue penetration. Photodynamic therapy (PDT) is an emerging therapeutic modality that employs a non-toxic light-sensitive drug (photosensitizer) in combination with light to produce reactive oxygen species and destroy nearby cancer cells. Several studies explored photodynamic pre-treatment as a way to enhance nanomedicine delivery to the tumor, but the utility and mechanism of this approach has not been fully realized.

In our current work, we employed a low-molecular-weight (<2 kDa) porphyrin photosensitizer targeting prostate-specific membrane antigen (Porphy-PSMA) in combination with sub-therapeutic near-infrared (NIR) laser irradiation to enhance tumor nanoparticle delivery. Presently, we have demonstrated that Porphy-PSMA-enabled PDT pre-treatment enhanced and accelerated accumulation of organic nanoparticles (100 nm liposomes and 20 nm lipoproteins) in PSMA-positive subcutaneous mouse model. Furthermore, this approach enhanced tumor delivery of 50 nm gold

nanoparticles from 0.78 ± 0.46 %ID/g to 2.5 ± 0.27 %ID/g at 3 hours post-nanoparticle administration, as demonstrated by inductively coupled plasma mass spectroscopy. We are currently investigating the effects of targeted PDT pre-treatment on nanoparticle intra-tumoral distribution via 3D imaging of optically transparent intact tumors as well as histological analysis.

The low molecular weight of Porphy-PSMA allows it to homogeneously distribute within the tumor and its combination with targeted PDT opens access to the deep layers of tumor tissue for larger drug-carrying nanomedicines. This approach has a potential to enhance tumor accumulation and therapeutic efficacy of FDA-approved nanoformulations.



Combining strengths of low-molecular-weight agents and nanoparticles with targeted PDT pre-treatment.

COLL 455

Novel catalytically active gold nanocrystals electrochemically grown in water by a continuous method

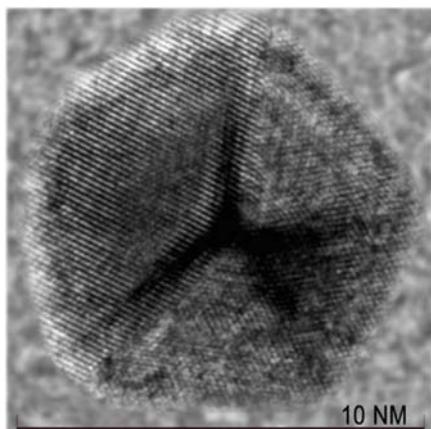
Mikhail Merzlyakov, mikhail.merzliakov@clenenanomedicine.com, Adam Dorfman, David K. Pierce, David Bryce, Mark Mortenson. Clene Nanomedicine, Inc., North East, Maryland, United States

We present a novel, continuous electrochemical nanocrystalline synthesis method to grow clean-surfaced highly faceted gold nanocrystals (GNCs) in water. The resulting GNCs have surfaces that are free of organic residues (e.g., are surfactant-free and capping agent-free). An AC current is applied to pairs of gold electrodes that are partially submerged in a flowing aqueous solution. The gold nanocrystals grow near the submerged electrode surfaces. The continuous process is scalable and does not require the use of any harmful organics, making it a green process. Important production control parameters include water flow rate, voltage, frequency, electrode current density, and ion content in the flowing aqueous solution. Control of these

parameters affects nanocrystal size, shape, and size distribution as characterized by transmission electron microscopy.

The resulting GNCs have crystalline structures that exhibit multiple twinned (111) crystal planes. The absence of organic residues on the crystal surfaces results in GNCs with superior catalytic activity when compared to gold nanoparticles of similar size made by the chemical reduction of HAuCl_4 .

We demonstrate that these novel GNCs oxidize nicotinamide adenine dinucleotide from NADH to NAD^+ at a significantly higher rate than common gold nanoparticles. In addition to superior catalytic activity and lack of toxicity, these GNCs are stable for more than a year even when concentrated to 1 mg/mL. Together, these properties make these novel GNCs particularly well-suited to biomedical applications.



COLL 456

Electrochemically grown, clean surfaced gold nanocrystals exhibit a very favorable safety profile in rodents, canines, and humans

Adam Dorfman, adam@clene.com, **Michael Hotchkin**, **Mikhail Merzliakov**, **Glen Frick**, **Mark Mortenson**. Clene Nanomedicine, Inc., North East, Maryland, United States

A significant challenge to the clinical use of gold nanocrystals in humans is the reported toxicity from animal and *in vitro* cytotoxicity studies. The surface chemistry of nanomaterials has been well-characterized and found to contribute to the toxicity profile of these materials. Here we describe the surface chemistry characterization and the clean toxicity profile of clean-surfaced, faceted gold nanocrystals produced in water using a novel electrochemistry method. Because these nanocrystals do not contain any capping agents, residual reactants, and/or stabilizing molecules, they exhibit improved toxicity and tolerability profiles compared to, for example, gold salts, when administered orally up to 90 mg/kg/day in animals and in doses up to 90mg/day in healthy adult volunteers. The surfaces of the gold nanocrystals have been interrogated with Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), high-angle annular dark-field scanning transmission electron microscopy scanning tunneling electron microscopy (HAADF-STEM), and X-ray photoelectron spectroscopy (XPS). These characterization data support the absence of any organic agents or oxides on the surfaces of the gold

nanocrystals. A 9-month chronic canine study with a four-week recovery concluded that the no-observed-adverse effect level (NOAEL) was the highest dose tested at 10 mg/kg/day, while a 6-month chronic rat study with 4-week recovery similarly concluded that the NOAEL was the highest dose tested at 40 mg/kg/day. In a Phase 1, first-in-human healthy subject study, the incidence of treatment emergent adverse events (TEAEs) was comparable between the treatment and placebo groups after 21 days of once daily oral administration. All TEAEs were mild in severity with none being severe or resulting in treatment discontinuation. All routine clinical laboratory assessments, vital signs, ECGs, and physical examinations did not reveal clinically notable findings. Based on these results, we conclude that the absence of surface organic residues is critical to the safety and tolerability of nanotherapeutics. This data represents the most comprehensive human drug safety profile to date for an orally administered clean surface gold nanocrystals.

COLL 457

SERS nanoparticles in medicine: New opportunities for spectroscopic cancer detection and image-guided surgery

Shuming Nie¹, nies@illinois.edu, Lucas A. Lane², Ruiyang Xue¹. (1) University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (2) Nanjing University, Nanjing, Jiangsu, China

Nanotechnology is an area of considerable current interest in biomedical engineering because of its broad applications in biomedical imaging, in-vitro diagnostics, and targeted therapy. The basic rationale is that nanometer-sized particles such as quantum dots, colloidal gold, and polymeric nanomicelles have functional and structural properties that are not available from either discrete molecules or bulk materials. When conjugated with targeting ligands such as monoclonal antibodies, peptides or small molecules, these nanoparticles can be used to target malignant tumor cells and the tumor microenvironment (such as tumor stroma and tumor vasculatures) with high specificity and affinity. In the “mesoscopic” size range of 10-100 nm, nanoparticles also have large surface areas for conjugating to multiple diagnostic and therapeutic agents, opening new possibilities in imaging, therapy, and surgery. At the present, however, there are several fundamental problems and technical barriers that must be understood and overcome. In this talk, I will discuss the major challenges and opportunities in the development of nanomedicine for intraoperative cancer detection and image-guided surgery.

COLL 458

Optically activated nanomedicines

Tayyaba Hasan, thasan@mgh.harvard.edu. Wellman Center for Photomedicine, Massachusetts General Hospital/Harvard Medical School, Boston, Massachusetts, United States

Optical activation of materials leads to thermal, photochemical and radiative processes. These can be captured for response-based therapeutic design. The ability to use light as a reagent to control drug release further allows for fabrication of multiagent constructs that attack multiple pathways making the nanomedicines more effective against cancer. Strategies for syntheses and applications in biology and medicine will be discussed.

COLL 459

Patient-tailored immunotherapies enabled by multimodal ImmunoPET-Raman imaging

Rizia Bardhan^{1,2}, rizia.bardhan@vanderbilt.edu, Yu-Chuan Ou³, Anita Mahadevan-Jansen², Todd E. Peterson², Michael Nickels², Henry C. Manning². (1) Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee, United States (2) Vanderbilt Ingram Cancer Center, Vanderbilt University Medical Center, Nashville, Tennessee, United States

The upregulation of immune checkpoint programmed death protein-1 (PD-1) expressed on CD8+ activated T cells, and interaction of PD-1 with its ligand, PD-L1, strongly contributes to an immunosuppressive tumor microenvironment (TME). Blockade of PD-L1 with therapeutic antibodies have shown long-term survival in many cancer patients and several clinical trials are ongoing. However, 75% of patients do not respond to PD-L1 blockade, in part due to inaccurate identification of PD-L1 expression in tumors incurring high costs of immunotherapy and toxicities in patients. Therefore, a compelling need exists for high resolution noninvasive detection techniques that will accurately detect PD-L1 and simultaneously identify other immunomarkers that show engagement of the immune TME. In this work we address this unmet clinical need with an innovative immunoPET-Raman multimodal imaging platform using novel immunoactive gold nanostructures (IGNs). IGNs are biocompatible ~55 nm gold nanostars labeled with antibodies, Raman-active molecules, and Cu⁶⁴ radiotracers. ImmunoPET-Raman enabled by multifunctional IGNs combines the depth-resolved whole body imaging of PET with high spatiotemporal resolution and multiplexing of surface-enhanced Raman imaging. Here we simultaneously track PD-L1 and CD8 (cluster of differentiation 8), which is expressed in effector T cells, with IGNs mediated ImmunoPET-Raman imaging to allow rapid assessment of PD-L1 status and longitudinal analysis of CD8+ engagement in the tumor microenvironment *in vivo*. Longitudinal imaging demonstrated maximum accumulation of IGNs in tumor occur 12h post intraperitoneal delivery and showed strong correlation between PET and Raman. Histology, transmission electron microscopy, and inductively coupled plasma mass spectrometry (ICPMS) of tissues was performed to evaluate IGNs bioavailability, toxicity, and clearance from tissues. Our *in vivo* study was combined *ex vivo* Raman spatial maps of whole tumor lesions that provided both a qualitative and quantitative assessment of biomarker status with near cellular-level resolution. High resolution SERS maps also provided an overview of MGNs distribution in tumors which correlated well with the vascular density. This study demonstrates ImmunoPET-Raman mediated by IGNs provides an accurate measure of

multiple biomarkers both *in vivo* and *ex vivo* which will ultimately enable a clinically-translatable platform for patient-tailored immunotherapies and combination treatment.

COLL 460

Biomedical applications of porphyrin-phospholipid liposomes

Jonathan F. Lovell, *jonathanflorell@gmail.com*. University at Buffalo, Buffalo, New York, United States

Porphyrin nanovesicles have been developed that can release drugs in response to red laser irradiation, leading to enhanced drug deposition in irradiated tumors. Inclusion of 2 molar % porphyrin-phospholipid (PoP) imparts optimal near infrared (NIR) light-triggered release of doxorubicin (Dox) from conventional sterically stabilized stealth liposomes. Dox in stealth PoP liposomes has a circulation half-life in mice of 21.9 hours and is stable in storage for months. Following intravenous injection and NIR irradiation, Dox deposition increases ~7 fold in treated subcutaneous xenografts. A low dose 3 mg/kg Dox phototreatment with stealth PoP liposomes was more effective than a maximum tolerated dose of free (7 mg/kg) or conventional long-circulating liposomal Dox (21 mg/kg). These liposomes are effective at physiologically relevant dosing of 2 mg/kg in orthotopic models of breast cancer in rodents.

Second, these porphyrin nanovesicles can be chelated with cobalt for simple functionalization using polyhistidine ligands. Methods to attach polypeptides to lipid bilayers are often indirect, ineffective and can represent a substantial bottleneck in the formation of functionalized lipid-based materials. Although the polyhistidine tag (his-tag) has been transformative in its simplicity and efficacy in binding to immobilized metals, the successful application of this approach has been challenging in physiological settings. Here we show that lipid bilayers containing porphyrin-phospholipid that is chelated with cobalt, but not other metals, can effectively capture his-tagged proteins and peptides. The binding follows a Co(II) to Co(III) transition and occurs within the sheltered hydrophobic bilayer, resulting in essentially irreversible attachment in serum or in million-fold excess of competing imidazole. Using this approach we anchored peptides and proteins into the liposome for spontaneous nanoliposome-antigen particleization (SNAP) adjuvants, which show 10,000 more potency than other adjuvants for a malaria antigen of interest.

COLL 461

Molecular afterglow imaging of semiconducting polymer nanoparticles

Kanyi Pu, *kypu@ntu.edu.sg*. School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore

Optical agents with long-lasting light after cessation of excitation have great promise for ultrasensitive *in vivo* imaging due to eliminated tissue autofluorescence. However, such

imaging agents are rare and generally limited to inorganic nanoparticles with relatively low brightness and short near-infrared (NIR) emission. In this study, we introduce a new generation of purely organic agents based on semiconducting polymer nanoparticles (SPNs) that can store photon energy via chemical defects and then emit long NIR afterglow luminescence at 780 nm after light irradiation. The *in vivo* afterglow of SPNs is more than two orders of magnitude brighter than that of concentration-matched inorganic agents, and the signal is detectable through an entire live mouse—a feat that is nearly impossible with NIR fluorescence imaging. Such a high sensitivity couple with the ideal biodistribution allow SPNs to rapidly detect xenograft tumors with the size as small as 1 mm³ and tiny peritoneal metastatic tumors that are almost invisible to naked eye. Moreover, the structural versatility of SPNs enables a smart activatable afterglow probe with signal specific to the presence of biothiols permitting excitation-free real-time imaging of drug-induced hepatotoxicity in living mice. This study provides the basis for an entirely new class of optical reporters for molecular imaging at a sensitivity level not achievable with conventional NIR fluorescence imaging.

COLL 462

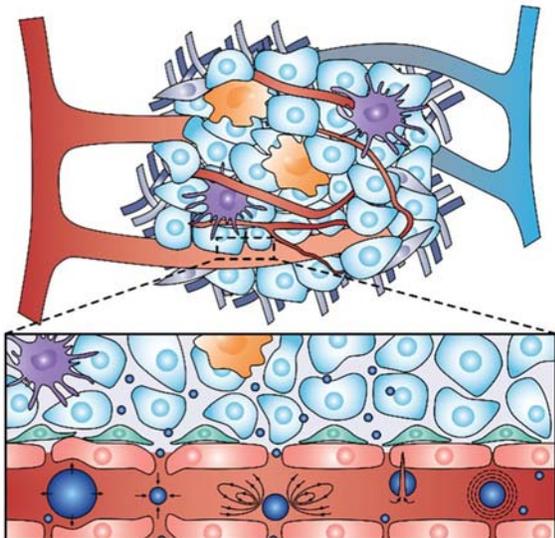
Ultrasound-triggered micro-to-nano conversion: Extending porphyrin-bubble theranostic potential beyond the vasculature

Carly Pellow^{1,2}, carly.pellow@gmail.com, David Goertz^{3,2}, Gang Zheng^{1,2}. (1) University Health Network, Toronto, Ontario, Canada (2) Medical Biophysics, University of Toronto, Toronto, Ontario, Canada (3) Sunnybrook Research Institute, Toronto, Ontario, Canada

Photodynamic therapy is a minimally invasive strategy with potential to target infiltrative tumours. However, reliance of nanoscale photosensitizers on passive targeting has resulted in insufficient delivery, prompting an exploration of ultrasound-stimulated microbubbles (MBs) to actively enhance permeability. Recently, novel porphyrin photosensitizer-shelled MBs demonstrated an ultrasound-triggered conversion to porphyrin nanobubbles (NBs). In addition to photoactive porphyrin, the presence of gas in the daughter NBs opens the possibility of stimulating further bubble-mediated ultrasound imaging and therapy beyond the vasculature.

While MB behaviour in the vasculature is well-established, the effects of size and a confining environment remain relatively unexplored. Vessel and tissue phantom studies have explored acoustic emissions from MB and NB populations, demonstrating higher resonant frequencies, distinct pressure-dependent activity thresholds, and sustained signals for constrained NBs. Despite elevated resonance frequencies and thresholds, porphyrin NBs were detectable *in vivo* in a KHT mouse model at clinically relevant frequencies. We have further gained insight into the spatiotemporal extravasation of NBs with transducers integrated into a two-photon window-chamber microscopy setting. This enables acoustically induced conversion and fluorescence tracking of porphyrin-NB extravasation in a setup that is uniquely poised to investigate the cavitation and phototherapeutic potential of porphyrin-NBs directly in the intra-tumoural space. Work to-date demonstrates differences in bubble behaviour as a function of size and

surrounding environment and highlights unique characteristics of nanobubbles for imaging and therapeutics beyond the vasculature.



While microbubbles are confined to remain in the vasculature, physiological consequences of tumour microvasculature afford opportunities for nanoscale agents to escape the intravascular space and expand bubble-mediated imaging and therapeutic potential.

COLL 463

Remotely targeted and triggered nanomedicine

Daniel S. Kohane, daniel.kohane@childrens.harvard.edu. *Anaesthesia, Boston Children's Hospital, Harvard Medical School, Newton, Massachusetts, United States*

Remotely targeted and triggered drug delivery systems involving the nanoscale have become areas of considerable interest in nanomedicine. This talk will review the rationales for such systems and their characteristics, when used for local or systemic drug delivery. Examples will be provided of applications in cancer, pain, and diabetes, using a variety of external energy sources as triggers. Comparisons will be provided to non-triggered and non-nanoscale systems. The much-debated issue of the depth in tissue at which drug delivery systems can be triggered will be discussed.

COLL 464

From molecules to mammals: Inventing luminescent nanoparticles for biology

Gang Han, gang.han@umassmed.edu. *Biochemistry and Molecular Pharmacology, University of Massachusetts-Medical School, Worcester, Massachusetts, United States*

Functional luminescent nanoparticles are promising materials for in vitro and in vivo optical imaging and therapy due to their unique optical and chemical properties. In this

talk, I will present three new types of biocompatible luminescence nanoparticles that were invented in our lab. The first type of materials is upconversion nanoparticles (UCNPs). I will present new developments regarding engineering UCNPs towards photodynamic therapy, optogenetic applications in neuroscience and immunotherapy. The second type of nanoparticles is persistent luminescence nanoparticles (PLNPs). They are bioluminescence-like and possess unprecedented in vivo deep tissue energy rechargeability, outstanding signal-to-noise-ratio with no need for an excitation resource (light) during imaging, and they can be directly detected with existing imaging systems. These nanoparticles continue to emit light for minutes or hours and, in some cases, days, after turning off the excitation source. These long-lasting, light-emitting nanocrystals can provide noninvasive imaging technology for evaluating structural and functional biological processes in living animals and patients. The third is a type of organic Bodipy nanoparticles that were tailored with outstanding NIR absorbing ability. Rather than the conventional laser light needed in PDT, I will present their ultralow power lamp operable PDT applications in deep tissue tumor treatment.

COLL 465

Design and preparation of near infrared absorbing BODIPY nanoparticles: Applications in photodynamic therapy

Ling Huang, ling.huang@umassmed.edu. Biochemistry and Molecular Pharmacology, University of Massachusetts Medical School, Worcester, Massachusetts, United States

Tissue penetration depth is a major challenge in practical photodynamic therapy (PDT). A biocompatible and highly effective near infrared (NIR)-light-absorbing carbazole-substituted BODIPY (Car-BDP) molecule is reported as a class of imaging-guidable deep-tissue activatable photosensitizers for PDT. Car-BDP possesses an intense, broad NIR absorption band (600–800 nm) with a remarkably high singlet oxygen quantum yield ($\Phi_{\Delta} = 67\%$). After being encapsulated with biodegradable PLA-PEG-FA polymers, Car-BDP can form uniform and small organic nanoparticles that are water-soluble and tumor-targetable. Rather than using laser light, such nanoparticles offer an unprecedented deep-tissue, tumor targeting photodynamic therapeutic effect by using an exceptionally low-power-density and cost-effective lamp light (12 mW cm^{-2}). In addition, these nanoparticles can be simultaneously traced in vivo due to their excellent NIR fluorescence. This study signals a major step forward in photodynamic therapy by developing a new class of NIR-absorbing biocompatible organic nanoparticles for effective targeting and treatment of deep-tissue tumors. This work also provides a potential new platform for precise tumor-targeting theranostics and novel opportunities for future affordable clinical cancer treatment.

COLL 466

Drug delivery for ovarian cancer: The role of surface chemistry and administration route for targeting therapeutics with layer-by-layer nanoparticles

Santiago Correa¹, sancor@mit.edu, **Natalie Boehnke**¹, **Antonio Barberio**³, **Mohiuddin A. Quadir**², **Erik C. Dreaden**¹, **Paula T. Hammond**⁴. (1) MIT, Cambridge, Massachusetts, United States (2) Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota, United States (3) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (4) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

This work aims to systematically study the role of surface chemistry and administration method in nanoparticle biodistribution in an orthotopic model of high-grade serous ovarian cancer (HGSOC). Despite the significant capabilities of nanoparticle drug carriers, the clinical translation of anticancer nanomedicine has lagged behind expectations. Difficulty in translating these systems stems in large part from the overreliance of in vitro cell culture assays as well as in vivo models of cancer that bear little resemblance to actual disease. And as a result, little systematic work has been performed to probe material characteristics that may overcome major physiologic barriers that impede the accumulation of nanoparticles into diseased tissue, such as the identification of characteristics that promote nanoparticle transcytosis through endothelial layers.

Our systematic approach takes advantage of the layer-by-layer assembly technique to generate nanoparticles with unique surface chemistries by varying the identity of the outermost layer. A small library of ten LbL nanoparticles was generated and screened for binding affinity to a panel of ovarian cancer cells in vitro, from which four candidate formulations were chosen for follow-up in vivo studies. Candidate formulations were administered either systemically or intraperitoneally in order to also study the impact of delivery route in tumor accumulation. Our findings confirm prior reports of low on-target accumulation of systemically injected nanoparticles in advanced orthotopic models of cancer, regardless of surface chemistry. However, our results also indicate that intraperitoneal administration significantly and reproducibly improved on-target nanoparticle accumulation for all surface chemistries. Alongside these findings, we also report the role of surface chemistry on the cellular distribution of nanoparticles within the tumor, liver and spleen following intraperitoneal administration, as well as differences in therapeutic efficacy due to differences in surface chemistry.

COLL 467

Biologically inspired design consideration for polymeric anticancer nanomedicine

Santosh Aryal^{1,2}, saryal@ksu.edu, **Tuyen Nguyen**^{1,2}, **Arunkumar Pitchaimani**^{1,2}, **Ramesh Marasni**^{1,2}. (1) Chemistry, Kansas State University, Manhattan, Kansas, United States (2) Nanotechnology Innovation Center of Kansas State, Department of Anatomy and Physiology, Kansas State University, Manhattan, Kansas, United States

During the last several decades, controlled drug delivery technology has advanced significantly leading to the development of various clinical formulations improving patient compliance and convenience. Varieties of organic and inorganic nanomaterials have been extensively explored as a delivery system either in the form of drug carriers or imaging modalities. Of this system, one of the first FDA-approved nanomedicine is DOXIL[®], a PEGylated liposomal doxorubicin. This class of conventional nanomedicine relies on passive-drug targeting taking advantage of leaky tumor vasculature, called as Enhanced Permeability and Retention (EPR) effect. However, delivering the drug to the cancer cell in the tumor with heterogeneous microenvironment is highly challenging. To tackle these problems, attention has shifted towards the design of next-generation delivery vehicles with enhanced targeting functionalities for active delivery. In this talk, two different strategies to engineer active targeted drug delivery system will be discussed. First, a class of bone microenvironment targeted polymeric nanomedicine will be presented with various chemical approaches from polymer synthesis and lipid conjugation using Alendronic acid, a bone targeting ligand, as a building block of the design. Secondly, with the inspiration from the properties of the natural killer cell, state of the art cell membrane coated polymeric nanosystem for precise drug delivery will be implemented to achieve a high level of accumulation within the diseased tissue, improved circulation half-life, and minimal sequestration by the organs of the reticuloendothelial system. The talk will be concluded with the properties and finding of these engineered nanoconstructs including superior contrast enhancement properties for imaging, pharmacokinetics, and therapy.

COLL 468

Mutual prodrugs for treating aggressive neuroblastoma with biodegradable nanocarriers

*Ivan S. Alferiev, David Guerrero, Ferro Nguyen, Peng Guan, Venkatadri Kolla, Iliia Fishbein, Garrett M. Brodeur, **Michael Chorny**, chorny@email.chop.edu. Pediatrics, The Children's Hospital of Philadelphia, Philadelphia, Pennsylvania, United States*

BACKGROUND: Achieving optimal stability of carrier-drug association is key to the effective application of nanomedicines for treating adult and pediatric cancers. Re-engineering drug molecules into reversibly hydrophobized mutual prodrugs [co-drugs] is a new experimental strategy for improving nanocarrier-drug association, while allowing for controlled activation and synchronized release of mutually enhancing co-drug components. In this study, we focused on nanocarrier-based delivery of co-drugs formed with redox-silent tocol derivatives (mitocans) and topoisomerase I inhibitors of the camptothecin family, whose effective clinical use has been compromised by poor stability, incompatibility with conventional delivery vehicles and strong dose-limiting adverse effects. Nanocarrier-mediated delivery of co-drugs is designed to take advantage of enhanced intratumoral retention of sub-100 nm sized nanoparticles [NP], followed by co-drug activation in the tumor tissue.

METHODS AND RESULTS: A series of tocol co-drugs with a potent camptothecin analog, SN-38, constructed with progressively increasing activation rates were

encapsulated in biodegradable NP [85±36 nm] using a modified nanoprecipitation approach. NP loaded with a phenolic ester co-drug exhibiting the highest activation rate were also found to be most effective against chemo-naïve and chemoresistant neuroblastoma [NB] cells under conditions modeling different levels of NB cell exposure within the tumor. Phenolic carbonate and aliphatic ester designs were notably less efficient. In an *in vivo* model of previously untreated disease, nanocarriers with phenolic ester co-drug administered over 4 weeks [10 mg/kg, once a week] induced tumor regression and completely inhibited tumor growth over a 26-week period. The same co-drug/nanocarrier formulation tested against chemoresistant NB potently suppressed tumor growth and extended animal survival up to 7 weeks, in contrast to a marginal and transient effect of the clinically used SN-38 precursor, irinotecan [event-free survival of 3 weeks vs. 2 weeks in 'no treatment' and drug-free NP groups].

CONCLUSIONS: Camptothecin-mitocan co-drugs can be rationally designed as therapeutic cargoes for nanocarrier-based cancer therapy. The co-drug/nanocarrier combination strategy, whose feasibility and effectiveness against high-risk NB was demonstrated in the present preclinical studies, holds promise as a treatment for aggressive pediatric and adult solid tumors.

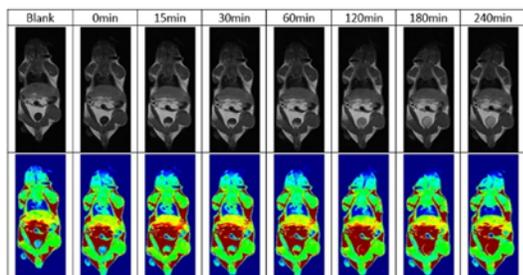
COLL 469

Gd-DTPA-dialkylamine with *o*-NO₂-benzylalcohol group: Synthesis and self-assembled behaviors for T₁-enhanced magnetic resonance imaging and light-controlled drug carriers

Chenyu Liu^{1,2}, yuyiity@163.com, Kai Ewert², Youli Li², Cyrus R. Safinya², **Weihong Qiao**¹, qiaowehong@dlut.edu.cn. (1) State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning, China (2) Material research laboratory, University of California Santa Barbara, Santa Barbara, California, United States

In the pharmaceutical field, drug carrier system holds great promises because they can change the ways that drug enters the body and enhance the absorption of drug. To increase efficiency and reduce side effects, we introduced a magnetic group (Gd-DTPA) to track its distribution in the body like a MRI contrast agent and a photocleavable group (*o*-NO₂-benzylalcohol) to break the vesicle by light to control drug release. The structure of Gd-DTPA-dialkylamine with *o*-NO₂-benzylalcohol (Gd-DTPA-ONB) was characterized by ¹H NMR, MS and FT-IR. Gd-DTPA-ONB not only showed an excellent surface activity, which CMC is around 1.2*10⁻⁴ mol/l, but also 7 days unchangeable size of vesicle by DLS. Surprisingly, MCF-7 cells still have 97% survival rate at 1.25mM of Gd-DTPA-ONB, which showed extremely low cytotoxicity compared with normal magnetic agent Gd-DTPA. Furthermore, anticancer drug doxorubicin was loaded into the hydrophilic cavity of vesicle with a high drug loading efficiency. The relaxivity time T₁ of Gd-DTPA-ONB vesicle showed four times longer than the clinical CA Magnevist (Gd-DTPA). In vitro, it could significantly enhance MRI imaging effect in the liver and kidneys of mice (shown in figure 1). Moreover, DLS, DIC microscope, TEM and ITMS-MS were used to verify the vesicle permitting controllable drug release by light. With the increasing of illumination time, the size of vesicle was becoming larger and larger, from

108nm to 937nm, which means the initial vesicle was broken by light and the piece of broken molecules reassemble themselves to form a larger and disordered vesicle. At the same time, doxorubicin was smoothly released. Therefore, the Gd-DTPA-ONB vesicle carrying doxorubicin serves as a theranostic nano-medicine to be capable of noninvasive imaging diagnosis, real-time imaging guidance and remote light-controlled therapy.

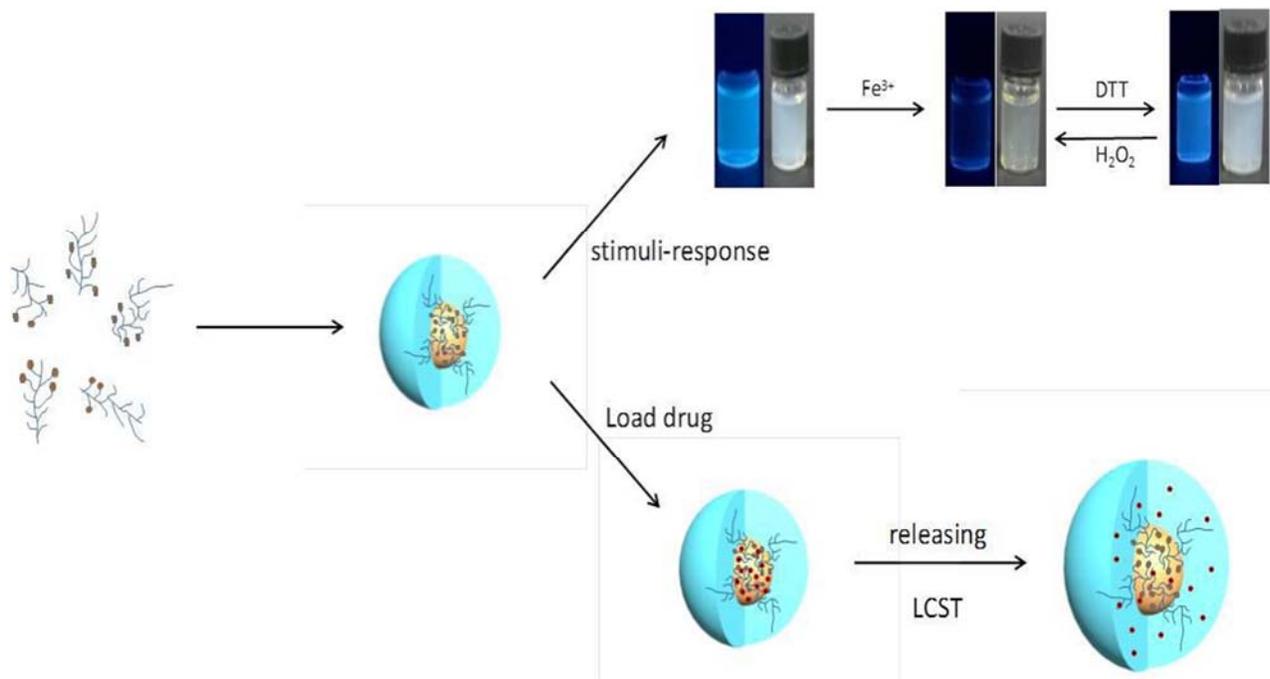


COLL 470

Multiple stimuli-responsive fluorescent micelles based on the self-assembly hyperbranched polymer for drug delivery and release

Min Xu¹, xumin@phy.ecnu.edu.cn, Huang Hailong². (1) School of Physics and Materials Science, East China Normal University, Shanghai, China (2) ECNU, Shanghai, Shanghai, China

Polymeric micelles, because of amphiphilic structure and self-assembly, have been widely studied for drug delivery and release. The ideal drug delivery micelles may carry the loaded drugs to targeted tissues and then controllable release the drugs. In this present work, a novel micelle with bright fluorescent emission and amphiphilic structure was prepared based on modified hyperbranched polymer. The amphiphilic hyperbranched polymers can form micelles with bright blue fluorescence via self-assembly in aqueous solution. The critical micelle concentration was 24.5 $\mu\text{g/mL}$ and the average size of micelle was 12.7 nm at room temperature. This fluorescent micelle shows a “turn on/off” of fluorescence with Fe^{3+} , DTT and H_2O_2 . In addition, the fluorescent micelle was thermal sensitive and the stimuli responsive temperature LCST is between normal temperature and fever as well as inflammation. As an example, this micelle system was exploited as a controlled-release system for treating fever symptom and the release behavior was investigated. The results show that the drug released more quickly at higher temperature and slowed down when the temperature back to normal. Hence, this micelle could serve as a promising candidate for all-in-one application of quantitative detecting, imaging, drug delivery, and targeted release.



The scheme of the self-assembly of polymeric micelles based on modified hyperbranched polymers, the “turn on/off” of fluorescence and the drug delivery and release.

COLL 471

Remotely controlled assembly and biocatalytic release of cargo molecules

Sergiy Minko¹, sminko@uga.edu, **Andrey Zakharchenko**¹, **Evgeny Katz**². (1) *The University of Georgia, Athens, Georgia, United States* (2) *Clarkson University, Potsdam, New York, United States*

In this presentation, we demonstrate a nature-inspired delivery system that explores assembling of nanocompartments/nanoreactors upon external signal (magnetic field). The ingredients of the nanoreactors are delivered by core-shell nanoparticles made of the magnetic core and block-copolymer brushes. The formation of the nanoreactor triggers biocatalytic reactions that results in release of the particle cargo. The specially designed stimuli-responsive biocatalytic system of superparamagnetic nanoparticles with a copolymer shell hosting the substrate and a complimentary enzyme is a powerful platform for remote control delivery and release of drugs and genetic materials. This delivery system combines the stimuli-triggered biocatalysis, remote control of biocatalysis and high selectivity of biocatalysis when only authorized biocatalytic reactions are triggered. The developed system provides an example of well-controlled magnetic field-triggered cancer drug release. The proposed platform is versatile and capable of delivery of various biological materials or therapeutic chemical molecules.

Mixing up better products in microgravity

Matthew Lynch, *lynch.matthew33@gmail.com. Corporate Research, Procter & Gamble Company, Cincinnati, Ohio, United States*

In the most-simple terms, we are trying to develop ways to formulate products that contain otherwise incompatible ingredients. We do this by creating microstructures in the fluid that keep these ingredients together to ensure the same great performance of the product from first to last use. To gain insight into the behavior of these microstructures, we replace commercial ingredients with larger, model colloids – to make them observable, but in doing so make them susceptible to other forces such as gravity. Removing gravity, allows us to learn about the microstructure in otherwise product-like conditions. This talk will highlight results from colloidal experiments on the International Space Station (ISS) in collaboration with NASA and CASIS at 240 miles above the surface of the Earth!

COLL 473

Research experiences at E Ink Corporation

Jay Anseth, *janseth@eink.com. E Ink Corporation, Billerica, Massachusetts, United States*

E Ink is the pioneer and commercial leader in ePaper technology. Our corporate philosophy focuses on delivering revolutionary products, excellent user experiences, and environmental benefits to the world's most influential brands and manufacturers, enabling them to install extremely durable, low power, daylight readable, and flexible displays in previously impossible or unimaginable applications. Our research and development department is a fast-paced, multidisciplinary organization comprised of scientists, engineers, and industrial designers who invent and implement our ePaper technology in consumer, industrial, medical, and architectural applications. E Ink R&D teams include a broad variety of science and engineering disciplines such as chemistry, colloid science, materials science, electrical engineering, physics, and computer science.

COLL 474

Working for a rapidly growing small company

Robert I. Maccuspie, *rob@n-icorp.com. Natural Immunogenics Corp., Sarasota, Florida, United States*

Natural Immunogenics Corporation has scientific career opportunities in various areas. Ranging from performing bench chemistry in the quality control laboratory environment, to developing and delivering scientific product education for medical professionals, there are different ways to contribute in this fast paced environment. NIC's Director of Science

will discuss his career path which has transitioned from government national labs, to program director and first faculty at a new university, to working for a small company, and offer brief perspectives on how experiences in each area better prepared the transition to an industrial career. Additional discussion will include one of the biggest challenges new graduates face at NIC, which is gaining experience working in an FDA-regulated GMP environment and fully understanding the effort and documentation required to maintain compliance. Working for a small, family-owned company provides many distinct benefits compared to larger corporations, while also presenting different opportunities and challenges.

COLL 475

Nanotechnology innovations and career opportunities at Savannah River National Laboratory

Simona Hunyadi Murph, *simona.murph@srnl.doe.gov. Savannah River National Laboratory, Aiken, South Carolina, United States*

The Savannah River National Laboratory (SRNL) is the applied research and development laboratory at the U.S. Department of Energy's (DOE) Savannah River Site (SRS). The laboratory applies state-of-the-art science to provide practical, high-value, cost-effective solutions to complex technical problems. This talk presents an overview of state-of-the-art nanotechnologies developed at SRNL. Specifically, I will describe how we are "putting nanoscience to work" for national security missions, environmental stewardship and clean energy applications. SRNL also offers high-quality career opportunities for young scholars to conduct cutting-edge research in the nanotechnology arena that enhance their professional skills and expand the Department of Energy's role in supporting scientific discovery and innovation. These unique career and internship prospects will be described in detail.

COLL 476

Wettability modification to enhance productivity in natural gas wells

Jimmie R. Baran, *jrbaran1@mmm.com. CRML, 3M, Prescott, Wisconsin, United States*

Fluid blockage occurs in natural gas wells in the near wellbore region. This fluid blockage could be aqueous-based from a high connate water level or aqueous based intervention (chemical treatment or waterflooding) and/or hydrocarbon liquid in the form of a retrograde condensate or volatile oil. The retrograde condensate or volatile oil is present due to an isothermal reduction in reservoir pressure. The greatest reduction in pressure occurs in the near wellbore region and across the face of a fracture. Materials have been developed to alter the wettability of the matrix and/or the wettability of the proppant in a fracture and thus increase the relative permeabilities of phases that come into contact with the treated area. This results in an increase in production over a longer period of time than is realized by more temporary solutions such as gas injection to

increase the pressure, solvents to clean up the blockage or fracturing. A summary of field trial data for these products will be presented.

COLL 477

How to train students to be independent scientists at Colgate

Long Pan, long_pan@colpal.com. Colgate Palmolive Co, Piscataway, New Jersey, United States

The Colgate-Palmolive Company is an American worldwide consumer products company founded in 1806. Colgate's commitment to three fundamental values: Caring, Teamwork and Continuous Improvement is part of everything it does, including developing individuals and teams. By better understanding the expectations of the consumer and customer, Colgate continuously works to innovate and improve its products, services and processes. The innovation heritage has been preserved and continues to flourish more than two centuries later.. To foster the innovative environment, all Colgate people are part of a global team sharing ideas and technologies and working effectively and efficiently throughout the world. The Research and Development (R&D) organization has responsibility for product development and new product launches that sustain profitable growth every year. One scientist, Long Pan, will introduce an intern program to illustrate how the R&D team cultivates the growth of young scientists to become independent and productive researchers. In addition, he will introduce a summer internship and a postdoctoral fellowship program developed at Colgate.

COLL 478

Research career at an army laboratory: Colloid and surface science research to support soldier performance optimization

Ramanathan Nagarajan, ramanathan.nagarajan.civ@mail.mil. Natick Soldier RDEC, Natick, Massachusetts, United States

Soldiers are the foundation of national defense. Only their ability to operate and dominate in future operating environments can guarantee the security of the country. The Army science & technology program focused on the Soldier is designed to ensure that the Soldier can perform optimally by taking advantage of the rapid developments in various material and non-material science/technology fields. A few examples of colloid and surface science applications that provide material technologies in support of the Soldier will be presented, including: surface chemistry on textile materials to develop chemical and biological protective garments; use of protein-polymer conjugates to inactivate chemical agents; and assemblies of colloidal nanoparticles to enhance efficient power harvesting from photovoltaic thin films. The research environment of the Army laboratories will be described. The research, development and engineering activities at an Army laboratory take place in close collaboration with academia and

industry. There are many opportunities for undergraduate and graduate students, post-docs and faculty to work in the Army laboratories as part of the R, D & E efforts. Some of these opportunities will be elaborated.

COLL 479

Development and integration of droplet-based microfluidic technologies into industrial research

Christopher Nelson, *cwnelson@dow.com*, *Nelie Loufakis*, *Kathryn Whitaker*, *Daniel Miller*, *Adam Schmitt*, *Adam Grzesiak*, *Carol E. Mohler*. *The Dow Chemical Company, Midland, Michigan, United States*

New knowledge and new technologies in the area of colloid and interface science are continuously being developed in universities across the world. However, transferring those tools, techniques, and associated know-how to industry can present a significant challenge. Through its University Partnership Initiative, The Dow Chemical Company collaborates with, and financially supports, leading academic programs, graduate students, and professors on focused, multi-year projects. Fundamental scientific research is leveraged against industry-relevant problems, while supporting the seamless transfer of technology and people from academia to careers in industrial research.

In this talk we will present a number of microfluidic tools and techniques that have been developed or inspired by work done through Dow Chemical's University Partnership Initiative. Specifically, we will focus on studies of droplet coalescence and emulsion stability in O/W and W/O systems, with applications in hard and soft surface cleaning, separation and recovery processes, water clarification, agrochemical formulation, and personal care product development.

COLL 480

Comprehensive screening of neuronal behavior on gradient micro-alignment topographies

Ryan McNaughton¹, *ryan8293@bu.edu*, *Yuda Huo*², *Guicai Li*¹, *Hengye Man*⁴, *Xin Zhang*³. (1) *Mechanical Engineering, Boston University, Boston, Massachusetts, United States* (2) *Biology, Boston University, Boston, Massachusetts, United States*

In the present study, we demonstrate a rapid and low-cost method, leveraging photolithographic and PDMS micromolding techniques, to design and prepare anisotropic, gradient micro-ridge/groove arrays with variable local pattern width. It was anticipated this study may demonstrate the ability of gradient micro-topographies to influence neuron adhesion, dendrite branching, and synapse formation, providing a comprehensive understanding of the cell-topography interaction for the design of neuroregenerative devices.

The surface topography of biomaterials with specific spatial structure mimic the physical microenvironment of neurons and regulate their orientation, neurite outgrowth and synaptic elements. However, most topographical structures used in neuron culture are fabricated with single geometries. This necessitates bulk fabrication, which is both inefficient and laborious, while also increasing potential contamination. A single gradient micro-topographical structure with a range of patterns begins to ameliorate these issues, although few studies have examined the influence of longitudinal micro-ridge/groove structures.

The physicochemical properties of the prepared gradient micro-ridge/groove arrays were characterized by analyzing the surface morphology and wettability. Cell experiments were subsequently carried out using primary rat hippocampal neurons. Following substrate fabrication, the patterning structure was confirmed to be intact and viable for cell contact. Additionally, cell adhesion was increased through surface treatment with poly-L-lysine and laminin, and verified through FTIR-ATR spectroscopy.

Immunofluorescent images of neurons in culture for 14 days revealed smaller pattern widths regulate neuron growth and increase orientation along the linear direction. Neurons cultured on these substrates demonstrate a preference to attach in areas of smaller pattern width. Additionally, cell somas located within a 5 μ m groove demonstrate heightened aspect ratios. Dendrites of these neurons extended less when introduced to a linear topography, decreasing their coverage area with respect to decreasing geometry. Finally, the density of synapses formed significantly decreased in the presence of topography. Thus, the effect of gradient micro-topography on neuron behavior was achieved and systematically understood by a one-step screening on a single integrated chip, lending itself to potential advances in the design of neuroregenerative micro-devices.

COLL 481

Dampening immune responses with polyphenol multilayer coatings for islet transplantation

*Veronika A. Kozlovskaya¹, Jessie M. Barra², Hubert Tse², **Eugenia P. Kharlampieva¹**, ekharlam@uab.edu. (1) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States (2) Department of Microbiology, University of Alabama at Birmingham, Birmingham, Alabama, United States*

For successful islet transplantation to restore glucose homeostasis in patients with Type 1 diabetes (T1D), there is a need for novel immunotherapies that can decrease innate immune-derived signals and mitigate adaptive immune responses involved in graft rejection. We hypothesized that encapsulation of pancreatic islets with a nanothin hydrogen-bonded multilayer coating of a natural polyphenol can provide an immunoprotective barrier to enhance islet allograft acceptance in mouse models of T1D. This cytoprotective coating consists of tannic acid (TA), an immunomodulatory

antioxidant, and poly(N-vinylpyrrolidone) (PVPON) and exhibits both antioxidant and immunomodulatory properties. The material is efficacious in modulating the redox state that can influence innate and adaptive immune maturation. We demonstrate that (PVPON/TA) coatings significantly decrease *in vitro* pro-inflammatory M1 macrophage responses including the generation of free radicals, cytokines (TNF- α , IL-12p70), and chemokines (CCL5 and CXCL10). Corroborating the diminution of chemokine synthesis, T cell trafficking was impaired in the presence of (PVPON/TA) coatings. (PVPON/TA) multilayer encapsulation preserves *in vivo* islet function as demonstrated by the restoration of euglycemia following transplantation into diabetic mice and was effective in delaying autoimmune rejection of transplanted islets. We will discuss the ability of this material to conjugate metalloporphyrin to further enhance immunomodulatory potential by dissipation of damaging free radicals involved in pancreatic islet graft rejection and immune maturation.

COLL 482

Synthesis and design of a biomimetic conductive nanocomposite for responsive wound management technology

*Heather R. Lange*¹, *Christian X. Loza*¹, *Lauren K. Werth*¹, *William E. Chura*³, **Jason J. Keleher**², keleheja@lewisu.edu. (1) Dept of Chem, Lewis University, Romeoville, Illinois, United States (2) Dept of Chem, Lewis University, Romeoville, Illinois, United States (3) Dept of Biology, Lewis University, Romeoville, Illinois, United States

Wound secretions can indicate the progression of healing through specific types of exudates from capillaries in the surrounding tissues due to increased capillary permeability. As the capillary walls expand, fluid enters the interstitial spaces and into the wound bed. This research incorporates a layered nanocomposite system comprised of a biomimetic hydrogel and conductive polymer layer. The secretions first diffuse through the hydrogel layer comprised of an alginate based system crosslinked with calcium ion and amino acids such as tryptophan and arginine. Structural diversity and intermolecular forces such as π - π stacking and hydrogen bonding have been found to impact the crosslinking of the hydrogel. As amino acids are the building blocks of proteins, their incorporation can therefore significantly improve upon the healing process by increasing adult human dermal fibroblast growth on the wound surface. To further optimize the gels, silver (Ag) and gold (Au) functionalized TiO₂ nanoparticles (NPs) were incorporated to enhance antimicrobial properties. Although Ag functionalized gels had high antimicrobial efficiency, Ag leached from the matrix, while the Au NPs provided inconsistent results. Due to drawbacks of the previously mentioned nanoparticles, attention has been shifted to copper (Cu) nanoparticles which lyse the bacterial cell membrane resulting in expulsion of cellular components while also exhibiting high conductivity. Once the hydrogel has reached maximum swelling capacity, the ions that have diffused into the conductive polymer layer increase the current through the polymer when a small voltage is applied. A correlation between swell capacity and conductivity was developed to determine the conductivity threshold needed to illuminate an LED. The conductive polymers of interest include polyaniline

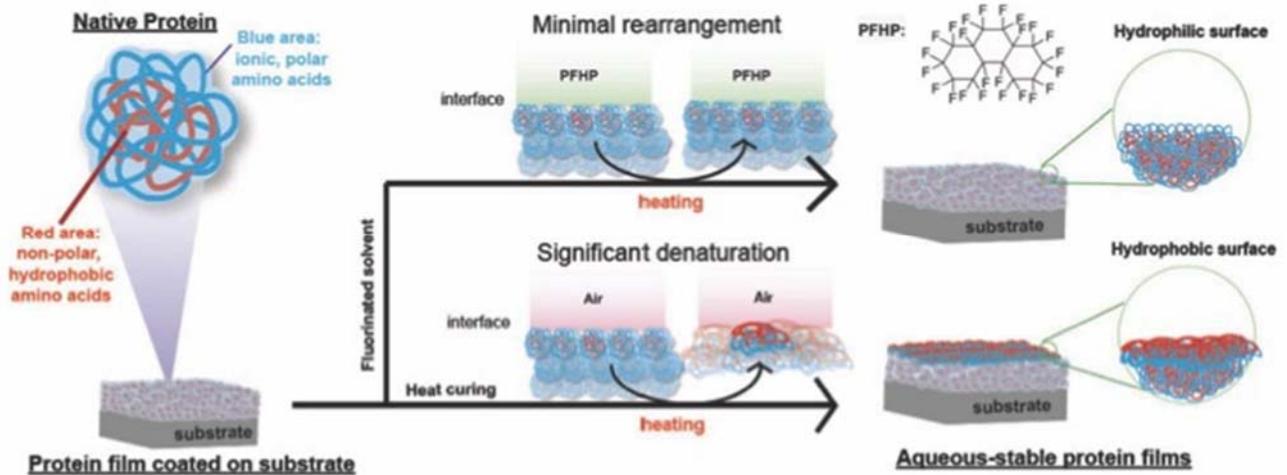
(PANI) and polypyrrole (PPy) due to their low cost and facile synthesis. Preliminary data has shown after 150 minutes on a simulated wound, the nanocomposite swelled over 150% and increased in 20% in conductivity.

COLL 483

Adaptation of charge and hydrophilicity of native protein on surfaces employing thermal treatment in fluoruous media

Sanjana Gopalakrishnan¹, sgopalakrish@chem.umass.edu, **Li-Sheng Wang**², **Yi-Wei Lee**³, **Jiaxin Zhu**⁴, **Stephen Nonnenmann**⁴, **Vincent M. Rotello**⁵. (1) Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States (2) Chemistry, University of Massachusetts Amhers, Amherst, Massachusetts, United States (3) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (4) Chemical Engineering, University of Massachusetts Amhers, Amherst, Massachusetts, United States (5) Univ of Massachusetts, Amherst, Massachusetts, United States

Protein-based materials provide a biocompatible and sustainable platform for the fabrication of functional materials for biological applications such as tissue engineering and controlled drug delivery. Current strategies to design stable protein films are limited due to a narrow range of self-assembling protein precursors, the use of toxic crosslinkers or heat-induced denaturation. A technique utilizing a wide range of protein precursors while retaining native protein properties, must be employed to design proteins films for a variety of applications. We have developed a scalable and additive-free thermal treatment for the fabrication of stable, hydrophilic protein films. In this approach, protein films are treated in the presence of a fluoruous media. Protein building blocks retain most of their secondary structure, enabling us to create charged films using charged native proteins. We demonstrate the versatility of this strategy through fabrication of antifouling coatings on complex three-dimensional surfaces, such as dental implants. The generation of highly biocompatible non-fouling surfaces and regulation of cellular adhesion through choice of protein precursor, proves that these films are viable candidates for use in biomaterials.



COLL 484

Investigating the morphological and mechanical properties of amyloid fibril formation using atomic force microscopy (AFM) for biomaterial applications

Sumeyra Gokalp, sumeyra.gokalp001@Umb.edu, Michelle C. Foster. Chemistry, University of Massachusetts Boston, Boston, Massachusetts, United States

Amyloid fibrils are irreversibly misfolded proteins. Several degenerative diseases in human beings are associated with different kinds of proteins that form into amyloid fibrils, e.g., Amyloid β -42 fibrils and Alzheimer's Disease. The driving forces and molecular mechanisms of amyloid formation are still unclear, but it is thought to be the same for all types of amyloidogenic proteins. Hen Egg White Lysozyme (HEWL) is a low-cost and widely recognized model protein, which we use to help understand the mechanisms of amyloid fibrillogenesis. We denature the HEWL protein under both acidic and neutral conditions; and monitor the growth of lysozyme amyloid fibrils under these conditions over a month period using Atomic Force Microscopy (AFM). AFM is a powerful single molecular technique to investigate fibril polymorphism, and it provides a topographical image of the fibrils bound to a mica substrate. Examining the AFM images taken after different incubation times, thus at various stages of growth, allow us to analyze their morphological and nanomechanical parameter differences, such as length, height, and Young's Modulus to better understand the growth mechanisms of amyloid fibrils under different conditions. Additionally amyloid fibrils have recently received much attention as advanced bionanomaterials for interesting applications in material science, nanotechnology, and biomedicine due to their intrinsic properties. This research focuses on the creation of easy, inexpensive, biodegradable, strong, and highly ordered amyloid fibrils using HEWL as a natural nanomaterial; arguably, a superior alternative to glass fiber composite materials that provides comparable performance.

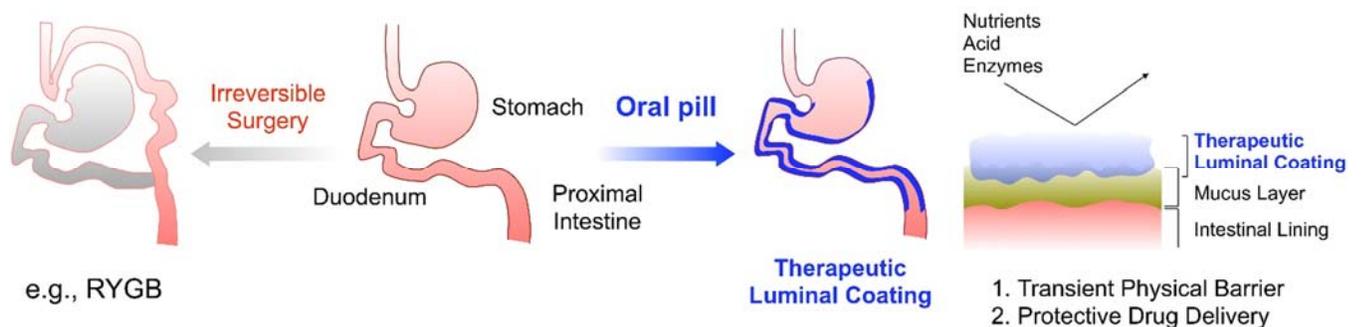
COLL 485

Therapeutic luminal coating of the intestine

Yuhan Lee, ylee21@partners.org. Medicine, Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts, United States

The gastrointestinal (GI) tract and specifically the small bowel are not only the principal site of nutrient digestion and absorption, but also one of the body's largest reservoirs of immunologically active and hormone-producing cells. As such, the intestine has been increasingly recognized as critical to the pathogenesis of systemic diseases, with substantial data highlighting the role of the small bowel as a therapeutic target for local and systemic diseases. The most notable of these observations have been data supporting the role of small intestine as a therapeutic target in type-2 diabetes (T2D). In Roux-en-Y gastric bypass surgery (RYGB), isolating the proximal bowel from nutrient exposure is a critical step in the metabolic success of this surgery leading to weight-independent improvement in T2D. Furthermore, many well-known diseases such as inflammatory bowel disease (IBD), affect the mucosal surface of the bowel yet direct drug delivery to the affected mucosa is challenging. Digestive characteristics in the proximal GI tract, specifically the acidity of the gastric lumen, prevent the ability to deliver many drugs, specifically potent biologics, directly to the intestinal mucosa. As a result, these agents are given systemically with increased side effects and challenges in administration. These diverse observations highlight the critical need to develop a therapeutic platform technology that can provide reliable access to the small bowel mucosa.

Here we describe the development of an orally delivered therapeutic platform that forms a transient physical coating on the bowel (**Figure 1**). The coating reduces nutrient exposure to the intestinal mucosa as indicated for T2D, and enables delivery of therapeutics (e.g., proteins, peptides), protected from gastric digestion, to affected intestinal mucosa. Through screening, we have identified and further engineered sucrose octasulfate aluminum complex. The engineered compound referred to as LuCl (*Luminal Coating of the Intestine*) can be orally administered, rapidly binds to the luminal surface of the small intestine, forms a continuous barrier coating to block nutrient contact, significantly lowers postprandial glucose response *in vivo*, and protects active biological agents from gastric acid exposure, allowing delivery to the duodenum and small intestine.



COLL 486

Hyaluronan density influences adhesion, morphology and migration of cancer cells

Ana M. Carvalho^{1,2}, Diana Soares da Costa^{1,2}, Rui L. Reis^{1,2}, Iva Pashkuleva^{1,2}, pashkuleva@dep.uminho.pt. (1) 3Bs Research Group, University of Minho, Barco - GMR, Portugal (2) ICVS/3B's – PT Government Associate Laboratory, University of Minho, Braga/Guimaraes, Portugal

Hyaluronan (HA) is a linear non-sulfated glycosaminoglycan present in the extracellular matrix and known to modulate cell-cell and cell-ECM interactions. In cancer, the synthesis, degradation and signaling of HA is altered. For instance, its main receptor, CD44, is overexpressed in several types of cancer and has been correlated with disease progression through cancer cell proliferation, migration and chemoresistance. Herein, we investigated the behavior of breast cancer cells with different CD44 expression and invasion profile on HA density gradients. These gradients were achieved by deposition of colloidal gold (Au) on amino-functionalized surfaces at different ionic strengths and following binding of end-on thiol modified HA on the Au. At low HA density, small number of adherent round cells were found for all studied cell lines. Cells adherent to the areas with high HA density presented a spindle-like morphology. The differences were more pronounced for cells overexpressing CD44. These cells also form long filopodia when adhered on areas with middle and high HA density. Of note, colocalization of CD44 and actin was observed at the filopodias edges. Cell motility was also affected by the gradient – at low densities cells presented higher motility, which decreased with the increase of HA density. Besides this common trend, we observed differences among the studied cells. CD44⁺⁺ cells had shorter persistent length displacement than CD44⁺ and CD44⁻ cells. Upon CD44 blockage, all types of cells (CD44⁺⁺, CD44⁺, and CD44⁻) behave similarly. These results suggest that cells recognize HA gradients through CD44 receptors and that the HA density can be used to sort cells with different expression of this receptor.

COLL 487

Photodegradable polyacrylamide gels for dynamic modulus control of cell culture platforms

Sam C. Norris, sammynorris@gmail.com, Jennifer Soto, Song Li, Andrea M. Kasko. 410 Westwood Plaza, Department of Bioengineering, Los Angeles, California, United States

Crosslinked polyacrylamide gels are a commonly used hydrogel in biotech and cell culture applications. These hydrogels are easily fabricated, with precise control of the material stiffness, using readily available materials, resulting in their widespread popularity. Furthermore, specific proteins or cell binding domains can be covalently attached to the surface of polyacrylamide hydrogels to allow for precise control of the chemical environment. However, once fabricated, the chemical and physical properties of polyacrylamide gels cannot be altered. To this end, we have developed a photodegradable polyacrylamide gel system that allows for dynamic control of the polyacrylamide gel stiffness with exposure to light. Photodegradable polyacrylamide gels were produced by copolymerizing acrylamide and a photocleavable *ortho*-

nitrobenzyl (*o*-NB) bis-acrylate crosslinker that was synthesized in our lab. Adhesive proteins were covalently attached using standard functionalization techniques for polyacrylamide gels. Cells were cultured on the surface of the gels and were exposed to light *in situ*. Upon polymerization, hydrogel networks were readily formed, where the initial stiffness could be precisely tuned by changing the concentrations of acrylamide and *o*-NB bis-acrylate molecules, respectively. When the hydrogels were exposed to light, the *o*-NB crosslinks cleaved and the stiffness of the photodegradable polyacrylamide gels decreased. We were able to control the dynamic range of the modulus by the exposure time and intensity of light. Fibroblast cells were successfully cultured on these materials and exhibited similar proliferation and viability to cells cultured on non-degradable polyacrylamide gels. *In situ* exposure of light reduced the modulus of the gels while maintaining cell attachment and viability. In this work, we have incorporated the simplicity and well-established protocols of standard polyacrylamide gel fabrication with the dynamic control of photodegradable systems. This will allow cell biologists and engineers to study more complex cellular behaviors that were previously inaccessible using standard polyacrylamide gels.

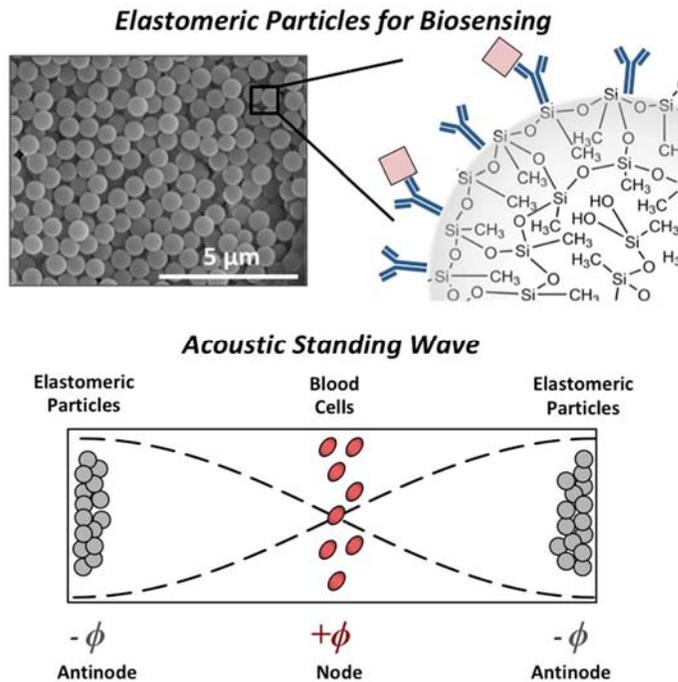
COLL 488

Elastomeric particles for cell and biomarker isolation in acoustofluidic devices

Wyatt Shields^{1,2}, cshields723@gmail.com, Korine A. Ohiri², Leah M. Johnson^{2,3}, Alice L. Li^{2,3}, Gabriel P. Lopez^{2,4}. (1) School of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts, United States (2) Biomedical Engineering, Duke University, Durham, North Carolina, United States (3) Research Triangle Institute, RTI International, Durham, North Carolina, United States (4) Chemical & Biological Engineering, University of New Mexico, Albuquerque, New Mexico, United States

The early detection of disease is critical to providing life-saving, therapeutic intervention. However, traditional methods for detection (e.g., tissue biopsy, endoscopy and medical imaging) can suffer from an elevated risk of complication, especially in elderly patients, and insufficient resolution to provide clear diagnoses. As such, many are looking toward “liquid biopsies” for clues into presence and status of different diseases due to its minimal invasiveness and ability to provide rich information about the native tumor or wound physiology. A critical first step in performing these analyses is the separation, enrichment and/or isolation of target biomarkers. In this talk, I will provide an overview of the new and exciting ways that elastomeric particles can accomplish this task via acoustically powered microfluidic (i.e., acoustofluidic) devices. Due to their low stiffness and density, elastomeric particles have negative acoustic contrast factors (Φ) in aqueous solutions, which allows them to focus along the antinodes of acoustic standing waves. In contrast, cells focus to the pressure node(s). Leveraging this disparity, I will describe two strategies to isolate specific biomarkers from non-target constituents in acoustofluidic devices. First, I will describe how elastomeric particles made from silicone monomers can be conjugated with biospecific antibodies to capture and isolate leukemia cells in acoustofluidic devices. Second, I will describe a strategy to modify the surfaces of elastomeric particles with genetically engineered polypeptides (i.e., elastin-

like polypeptides), which display lower critical solution temperature (LCST) phase behavior, to capture and acoustically isolate small molecules from blood. Together, these strategies provide a rapid, robust and gentle approach to continuously isolate rare biomarkers from inhomogeneous solutions in a convenient microchip device.



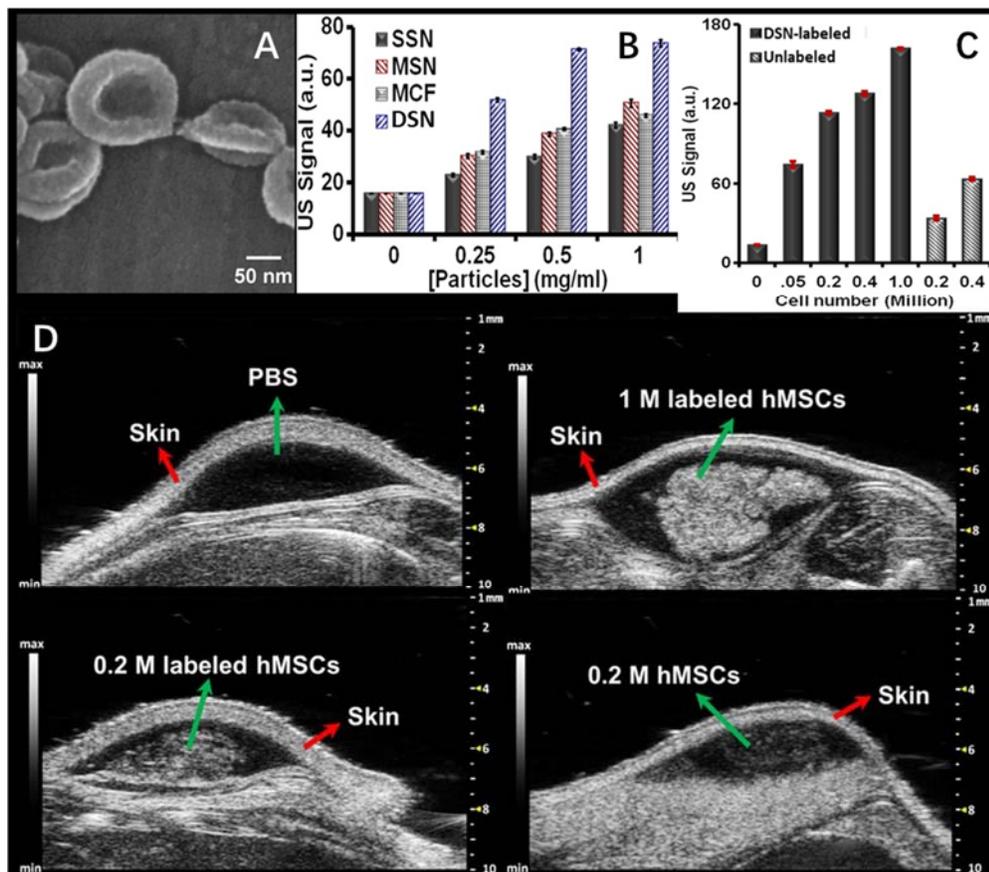
COLL 489

Discoid silica nanoparticles for stem cells tracking by ultrasound imaging

Fang Chen¹, fangch86@gmail.com, **Ming Ma**², **Junxin Wang**¹, **Shixiong Chen**², **Eric Zhao**¹, **Anamik Jhunjunwala**¹, **Sean Darmadi**¹, **Hangrong Chen**², **Jesse V. Jokerst**¹. (1) NanoEngineering, UCSD, La Jolla, California, United States (2) Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

The injection of stem cells to desired tissues and tracking them *in vivo* is crucial to understanding the mechanism of stem cell therapy and increasing efficacy. Ultrasound imaging offers video-frame-rates to guide stem cells injection into the desired tissues. However, it is difficult to track stem cells with ultrasound due to the poor contrast between injected stem cells and most soft tissues. Stöber and mesoporous silica nanoparticles have been demonstrated to increase the ultrasound contrast of stem cells. However, nanoparticles with higher echogenicity are needed to increase the LOD of stem cells *in vivo*. Here, we describe a novel silica nanoparticle reminiscent of red blood cells (SEM image is shown in **Figure 1A**). The ultrasound signal of discoid silica nanoparticles (DSN) at 0.25, 0.5, and 1 mg/ml was 2.25-, 2.39-, and 1.76-fold of that of Stöber mesoporous silica nanoparticles, 1.72-, 1.85-, and 1.46-fold of that of MCM-41 mesoporous silica nanoparticles, and 1.64-, 1.76-, and 1.62-fold of that of mesocellular

foam silica nanoparticles (**Figure 1B**). The DSN increased the echogenicity of human mesenchymal stem cells (hMSCs) by 3.63-fold *in vitro*. *In vivo* ultrasound images also demonstrated significant increase of echogenicity of transplanted DSN-labelled stem cells compared to unlabelled cells. DSN increased the *in vivo* echogenicity of hMSCs 3.3-fold times with 200,00 cells (**Figure 1C&D**). DSN decreased the theoretical LOD of hMSCs to 475 cells—nearly 50-fold lower than unlabelled cells.



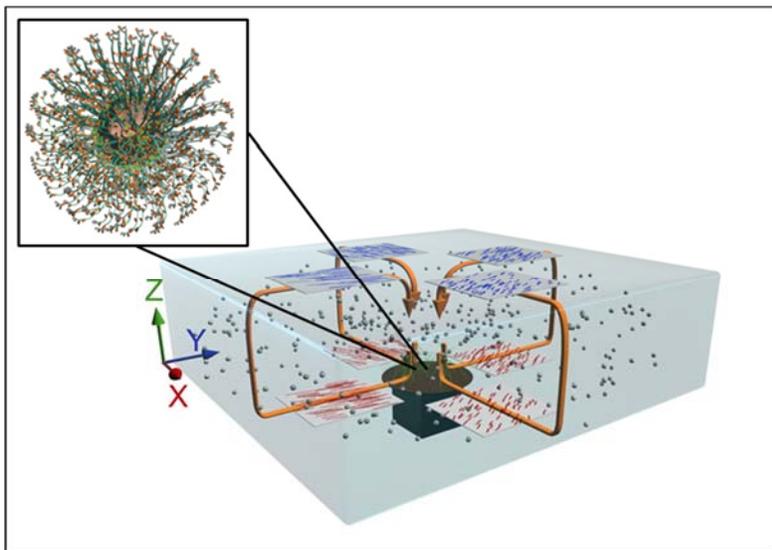
COLL 490

Phage colloids: Bacteriophages link enzymes to magnetic colloids for catalysis and micropumps

Mariana Alarcón-Correa^{1,2}, Jan-Philipp Günther^{1,2}, **Stefan Knoppe**², stefan.knoppe@ipc.uni-stuttgart.de, Jonas Troll^{1,2}, Vincent M. Kadiri^{1,2}, Dirk Rothenstein³, Joachim Bill³, Peer Fischer^{1,2}. (1) Micro, Nano and Molecular Systems Lab, Max Planck Institute for Intelligent Systems, Stuttgart, Germany (2) Institute for Physical Chemistry, University of Stuttgart, Stuttgart, Germany (3) Institut für Materialwissenschaft-Lehrstuhl für Chemische Materialsynthese, University of Stuttgart, Stuttgart, Germany

Self-propelled colloids are emerging as model systems for active matter. In the form of Janus structures, they are asymmetrically coated with a catalyst to function as chemical motors. It is desirable to replace the inorganic catalysts and the toxic fuels that are most often used with biocompatible enzymatic reactions. However, these are often less efficient. Here, we report a novel colloidal construct that makes use of bacteriophages and that exhibits very high enzymatic activities.

The immobilization of enzymes to inorganic supports often reduces the turnover rate of the enzymes. Nevertheless, inorganic surfaces and colloids offer many advantages for heterogeneous catalysis. For instance, magnetic colloids facilitate the recovery of the enzymes. We show that bacteriophages represent a proteinaceous microenvironment where the enzymes maintain the high activity typically found in homogeneous catalysis, and thus use the phages to link enzymes to magnetic colloids. We have genetically modified M13 bacteriophages such that they could be bound to the colloids via a His-tag. Due to the high aspect ratio and flexibility of the phages, it is possible to obtain a high local concentration of enzymes while ensuring the unhindered diffusion of substrate and product molecules. Enzymes were covalently bound to the main coat protein of the M13 bacteriophages, thus ensuring a high enzyme-coverage of the particles. The enzymes retained their activity over many catalytic cycles. The magnetic colloids permit the convenient recovery of the enzymes. Localizing these constructs with a magnetic field, allows the enzyme-bacteriophage-particle system to function as an enzymatic-micropump, where the enzymatic reaction generates fluid flow in a microchannel. Particle tracking was used to analyze the pumping effect of urease bound to the bacteriophages and it is shown that the colloidal bacteriophage system shows the fastest fluid flow reported by an enzymatic micropump to date.



Enzyme-phage-particle based micropumps.

COLL 491

Single-atom tailoring of metal nanoparticles

Rongchao Jin, *rongchao@andrew.cmu.edu*. Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Nanoparticles play a central role in the rapidly growing nanoscience and nanotechnology fields. Atomic level tailoring of nanoparticles is of great importance in order to map out the structure-property relationships. Recent success in the synthesis of atomically well-defined nanoparticles has offered exciting opportunities to pursue many fundamental issues that were difficult to tackle with polydisperse nanoparticles. This talk will present several cases of single-atom manipulations of metal nanoparticles, such as doping a single Ag or Cu atom into a gold nanoparticle and site-specific “surgery” of surface motifs of a nanoparticle. Such atomic-level manipulations provide unique opportunities for investigating how the structure and composition precisely impact the particle’s properties and functionality. New strategies for achieving such goals have been devised. Overall, the pursuit of single-atom level tailoring opens up new opportunities for controlling nanoparticles on an atom-by-atom basis.

COLL 492

Organic reaction catalysed by atomically precise metal nanoclusters

Manzhou Zhu, *zmq@ahu.edu.cn*. Anhui University, Hefei, China

Accompanied by the single-electron redox reactions, the phenylethanethiol-protected Au_{25}^- , Au_{25}^0 , and Au_{25}^+ nanoclusters can be reciprocally transformed with maintained structure. Taking the intramolecular cascade reaction on 2-nitrobenzonitrile for example, 2-nitrobenzonitrile is capable of capturing an electron from Au_{25}^- , which forms a free radical and further initiates the free radical reaction. Electron spin-resonance (ESR) spectra are employed to capture the signals of free radicals. In turn, excess NaBH_4 provides hydrogen source to reduce the 2-nitrobenzonitrile into 2-amniobenzamide, and further return Au_{25} to the negative state. It should be noted that the Au_{25} nanoclusters would not structurally change in this recycle system, but just function as an electron bridge to transfer the electron consistently. Furthermore, the Au_{25}^- nanocluster protected by selenophenol has been successfully obtained, which exhibits superiorly catalytic activity in reducing the *p*-nitrophenol. Moreover, doping the single Cd heteroatom to the $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^-$ nanocluster would significantly promote the efficiency in the oxidation of benzyl alcohol. On this basis, the synergistic effect between different metals in alloy nanoclusters has been precisely analyzed. Through analyzing the catalytic activity and selectivity on styrene propelled by Au-Ag bi-metallic nanoclusters, we conclude the catalytic role of Au, the selective role of Ag in the catalysis, and more obvious synergetic effect of surface-doped nanoclusters relative to nanoclusters with core-shell configuration. More importantly, the selectivity in oxidizing the styrene could be tailored by controlling the H_2O adsorption on the surface of nanoclusters. In addition, substituting the central atom of the $\text{Ag}_{25}(\text{SPhMe}_2)_{18}^-$ nanocluster with another metal atom (i.e., Pd, Pt, or Au) can remarkably influence the optical and electrochemical properties. Above-mentioned

results provide atom-level insights into the essence of catalysis induced by ultra-small nanoparticles.

COLL 493

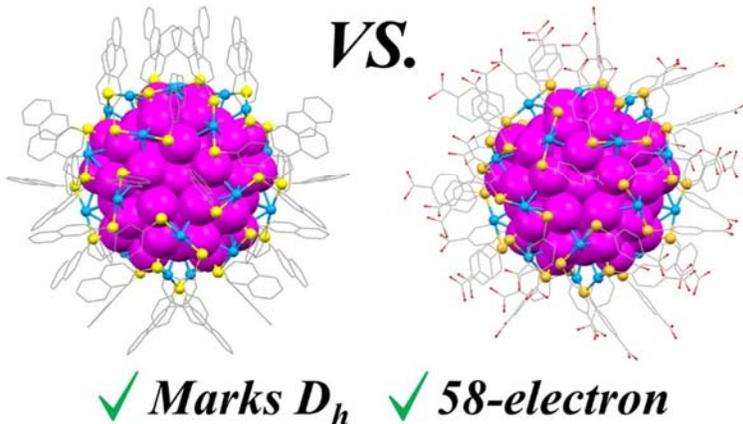
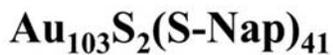
Tailoring the structure of 58-electron gold nanoclusters: Au₁₀₃S₂(S Nap)₄₁ and its implications

Tatsuya Higaki¹, thigaki@andrew.cmu.edu, Rongchao Jin². (1) Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

The structural analysis of atomically precise metal nanoclusters has been intensively studied by experimental and theoretical approaches. Significant progress has been achieved in X-ray crystallographic determination of thiolate-protected metal nanoclusters. However, critical questions are still missing clear answers. (i) The origin of stability for a Marks decahedral nanocluster has not been clarified; (ii) The correlation between the structure and optical property is still unclear, especially for large nanoclusters with more than 100 metal atoms.

In this presentation, I report the synthesis and crystal structure of a novel gold nanocluster with 103 gold atoms protected by 41 2-naphthalenethiolates plus 2 sulfidos, denoted as Au₁₀₃. X-ray crystallography reveals that the kernel of the new 58-electron nanocluster is a Marks decahedron of Au₇₉, similar to the previously reported structure in another 58-electron Au₁₀₂ nanocluster protected by 44 4-mercapto benzoic acids. This is a surprising observation given the totally different synthetic procedures and carbon tails in thiolate ligands, indicating the robustness of the decahedral structure as well as the 58-electron configuration. Despite the same kernel, the surface structure of Au₁₀₃ is quite different from that of Au₁₀₂, indicating the major role of ligands in dictating the surface structure.

Further studies on the property of Au₁₀₃ give us key information for elucidating the correlation between the structure and optical properties. For example, the DPV and NIR absorption spectrum reveal that the Au₁₀₃ has a similar HOMO–LUMO gap energy to Au₁₀₂, indicating the kernel is decisive for E_g, while the surface is less critical given the structural similarity in kernel and the difference in surface. In conclusion, this work illustrates the ligand-effected modification of the gold–thiolate interface independent of the kernel structure, which in turn allows one to map out the respective roles of kernel and surface in determining the electronic and optical properties of the 58-electron nanoclusters.



COLL 494

Molecular “surgery” and beyond: Understanding heterometal doping in atomically precise nanoclusters

Michael G. Taylor¹, mgt16@pitt.edu, Qi Li², Rongchao Jin², Giannis Mpourmpakis¹. (1) Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States (2) Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Heteroatom doping within atomically-precise thiolate protected nanoclusters has been experimentally shown to enhance nanocluster properties for specific applications. Although studies with electronic structure theory methods have shed light and led to accurate predictions of doping, little is currently known about the underlying physics responsible for doped nanocluster stability. Herein we highlight our recent work investigating dopant energetics, concentrations, and preferred locations with several bimetallic gold-based nanoclusters. Specifically, we reveal the charge state of dopant being an important factor determining the preferred dopant location. Additionally, we tied experimental doping observations to detailed thermodynamic energetics of nanocluster reactions with solution-phase precursor complexes. Finally, we show that dopant location and concentrations affect nanocluster stability, further expanding our recently developed “Thermodynamic Stability” theory from monometallic to bimetallic nanoclusters. Overall, this work furthers our understanding of doping energetics in atomically precise noble metal nanoclusters aiding in the prediction of experimentally synthesizable doped nanoclusters for targeted applications.

COLL 495

Structural and electronic characterization of CoO nanoislands on Au(111) using LT-STM

Ana Sanchez-Grande¹, Jonathan Rodriguez-Fernandez², **Esther Carrasco**¹, esther.carrasco@imdea.org, Koen Lauwaet¹, Jakob Fester², Rodolfo Miranda^{1,3}, Jeppe Lauritsen², David Ecija¹. (1) Surface Science, IMDEA Nanoscience, Madrid, Madrid, Spain (2) Interdisciplinary Nanoscience Center, Aarhus University, Aarhus, Denmark (3) Física de la Materia Condensada, Universidad Autónoma de Madrid, Madrid, Madrid, Spain

Low-temperature scanning tunneling microscopy (LT-STM) is known to be a suitable tool to investigate, at the nanometric scale, the structural and electronic properties of oxide surfaces in the form of thin films and nanostructures. Cobalt oxide nanoparticles have shown significant catalytic activity for the low temperature CO oxidation and the oxygen evolution reaction (OER) in the electrochemical water splitting. An improvement of the catalysts performance requires a controlled synthesis of the nanostructures as well as a deep understanding of the active phase and its surface chemistry. The preparation and characterization of model systems under vacuum conditions as well as a subsequent exposure to reactants under controlled conditions can be helpful in this sense. Following this methodology, CoO nanoislands supported on the Au(111) surface have been designed and employed to study the water dissociation using scanning probe and sample-average techniques. The different reported interaction of the water molecules with edge sites of the islands has been proposed to play a crucial role in the water oxidation reaction. However, an atomistic characterization of the electronic structure has been elusive. Here, we report a low temperature scanning tunneling microscopy and spectroscopy study of such a model system for water splitting. Our results show a complex structure within the oxide islands, which are characterized by a topographic and electronic Moiré, and some edge regions with distinct electronic fingerprints. In particular, the spectroscopic analysis show an increase of the valence band states at the borders of the islands and at the bottom moirons inside the nanoislands, whereas the oxygen dislocation lines have a higher density of states in the conduction band. Furthermore, a specific behavior towards water adsorption and dissociation of these sites is visualized and discussed. Thus, our study intends to open new avenues to understand and rationalized oxide nanostructures for energy related applications.

COLL 496

Enhancing nanoparticle catalysis for chemical transformations

Shouheng Sun, ssun@brown.edu. Brown University, Providence, Rhode Island, United States

Using MPd nanoparticles as examples, I will demonstrate that MPd NP catalysis can be further enhanced by synergistic NP-support interactions to achieve green chemistry conversions and syntheses. Studying 2 nm AgPd NP catalysis, we found that coupling AgPd NPs with 40 × 5 nm WO_{2.72} nanorods (NRs) made AgPd NPs catalytically more active for dehydrogenation of formic acid (TOF = 1718 h⁻¹ and E_a = 31 kJ/mol), and further for one-pot reactions of formic acid, 2-nitrophenol and aldehydes into

benzoxazoles in near quantitative yields. When a monolayer of 3 nm NiPd NPs were assembled on nitrogen-doped graphene (NG), these monolayer assembled NPs show maximum NiPd catalysis for the hydrolysis of ammonia borane (H_3NBH_3 , AB) with its TOF = 4896.8 h^{-1} and $E_a = 18.8 \text{ kJ/mol}$, and for one-pot synthesis of quinazolines in quantitative yields. The NiPd/NG catalyst show even higher activity for hydrodehalogenation of halogenated aromatics under mild reaction conditions, reducing mono-, di-, or even poly-halogenarenes to the corresponding dehalogenated arenes in >90% yield in 10% aqueous isopropanol solvent. Our studies demonstrate a reliable way of tuning NP-support synergistic effects to enhance NP catalysis for important chemical conversions and synthetic applications.

COLL 497

Metal and metal oxide nanoparticles encapsulated inside of zeolite crystals as highly efficient heterogeneous catalysts for chemical transformation

Feng-Shou Xiao, fsxiao@zju.edu.cn. Xixi Campus, Zhejiang University, Hangzhou, China

Here we show synthesis of core-shell structured metal and metal oxide@zeolite catalysts, which combine the advantages of both zeolite shape selectivity and metal high activity in catalytic reactions. For example, a manganese oxide catalyst with zeolite sheath (MnOx@S-1), which exhibits high selectivity for producing nitriles by efficiently facilitating the oxidative cyanation; when photocatalyst TiO_2 is fixed inside of zeolite crystals, it is given ideal performances for the selective degradation of pollutants but are harmless to the organisms; when Pd nanoparticles are encapsulated inside of zeolite crystals, it is shown high furan selectivity in the hydrogenation of biomass-derived furfural.

COLL 498

Controlled encapsulation of nanoparticle catalysts into nanoporous materials

Chia-Kuang Tsung, frank.tsung@bc.edu. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, United States

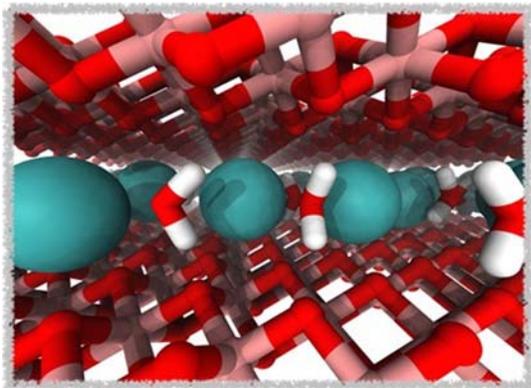
Towards our long-term vision of precisely controlling active sites, we focus on incorporating nanoparticle catalysts into crystalline nanoporous materials, metal-organic frameworks (MOFs). The precise molecularly-defined pores intrinsic to the MOFs provide a new tool to control the catalytic transformations on the catalysts. We have developed methods to combine organometallic catalysts, enzymes, and nanoparticle catalysts with MOFs of precisely tuned pore structures to manipulate the reactions.

COLL 499

Layer-by-layer assembly of colloidal nanosheets with individually differing properties to generate improved water oxidation catalysts

*Michael Zdilla*¹, mzdilla@temple.edu, *Ran Ding*¹, *Ian McKendry*¹, *Richard Remsing*¹, *Haowei Peng*², *John P. Perdew*², *Daniel R. Strongin*³, *Qing Kang*¹, *Akila Thenuwara*¹, *Eric Borguet*⁴, *Yaroslav Aulin*¹. (1) Chemistry, Temple University, Philadelphia, Pennsylvania, United States (2) Temple University, Philadelphia, Pennsylvania, United States (3) Temple Univ, Philadelphia, Pennsylvania, United States (4) Department of Chemistry, Temple University, Philadelphia, Pennsylvania, United States

A longstanding finding for manganese-mediated water oxidation reactions is that the manganese(III) oxidation state plays an important role in catalytic activity. The layered manganese oxide birnessite typically shows only residual water oxidation activity. However, guided by molecular dynamics and density functional theoretical calculations, controlled assembly of birnessite from colloidal nanosheets permits construction of an optimally designed birnessite with drastically improved catalytic capability in comparison to traditional synthetic birnessite. Synthesis, characterization, electronic structure, and reactivity of these systems will be presented in context of how theory and simulation has guided the design and understanding of their function.



The reactive interlayer of birnessite can be optimized for catalysis by control of interlayer water dynamics, and the average oxidation state of the top and bottom layers.

COLL 500

Transformation pathways of bimetallic nanoparticles at atomic scale

Yong Wang, yongwang@zju.edu.cn. Materials Science and Engineering, Zhejiang University, Hangzhou, China

Bimetallic nanoparticles have attracted considerable attention due to their potential applications in numerous fields of science and technology. Their shape, composition and structure, which have a significant impact on their properties, would be modified in

response to different thermal treatments. It is therefore essential to understand how the nanoparticles evolve during heating process at atomic resolution in order to design desired nanoparticles with particular shape and structure for different applications. In this talk, I will report our recent progress in the transformation behaviors of bimetallic nanoparticles during in-situ annealing by aberration-corrected scanning transmission electron microscopy and multi-scale modeling. The mechanism governing the transformation will be discussed in detail.

COLL 501

Multimetallic nanocrystals and their surface and interface electrocatalysis

Shaojun Guo, guosj@pku.edu.cn. Materials Science and Engineering, Peking University, Beijing, China

Engineering nanocrystals with size, shape, composition, structure and strain control is the key to enhance the performance of energy conversion devices. In this talk, I will focus on my recent advances in making/tuning high-quality metal-based nanocrystals for boosting the electrocatalysis of fuel cells and solar fuels. I will start with several examples on how to tune the surface and interface of multimetallic nanocrystals for achieving more efficient oxygen reduction electrocatalysis. Then, I will move to tune the defects and high-index facets of multimetallic nanocrystals for boosting the liquid fuels oxidation catalysis. Finally, I will discuss how to introduce the interface of metal-based materials for highly efficient hydrogen evolution reaction.

COLL 502

Fabrication and application of inorganic nanoparticle superstructures

Zhiyong Tang, zytang@nanoctr.cn. National Center for Nanoscience and Technology, Beijing, China

Fabrication of inorganic nanoparticle superstructures is one of the most important ways to realize the practical applications of nanomaterials in many fields, e.g., photonics, electronics and catalysis. In this talk, I will introduce the recent progresses in our group on this research topic, which include: (1) fabrication of large-scale and hierarchy superstructures via manipulation of the physical interactions between inorganic nanoparticle building blocks; (2) exploration of optical activity of the assemblies of chiral structures; and (3) application of inorganic nanoparticle superstructures in the field of catalysis and energy. At the end of the talk, I will briefly discuss current challenge in our work.

COLL 503

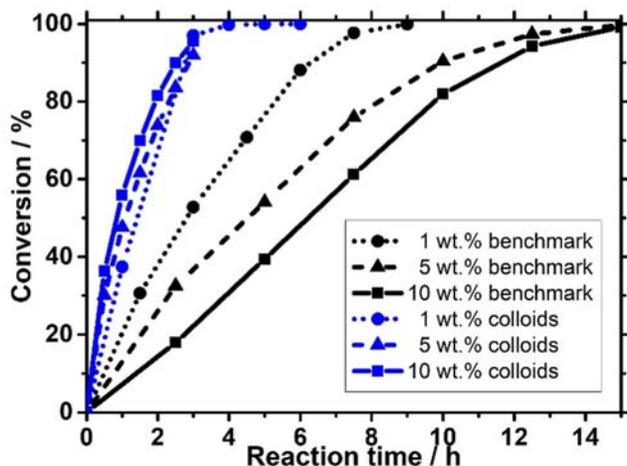
Solutions for catalysis: A surfactant-free synthesis of precious metal nanoparticle colloids in mono-alcohols for catalysts with enhanced performances

Jonathan Quinson¹, jonathan.quinson@chem.ku.dk, Sarah Neumann², Jan Bucher³, Masanori Inaba¹, Søren Simonsen⁴, Luise Theil Kuhn⁴, Mehtap Oezaslan⁵, Sebastian Kunz², Matthias Arenz³. (1) Chemistry, University of Copenhagen, Copenhagen, Denmark (2) Institute of Applied and Physical Chemistry, University of Bremen, Bremen, Germany (3) Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland (4) Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark (5) School of Mathematics and Science, Carl von Ossietzky Universität, Oldenburg, Germany

To optimize precious metal nanocatalysts, an optimal set of nanoparticle (NP) properties (*composition, size, loading, etc.*) must match specific operating conditions. Synthesis routes offering independent control on NP properties are then highly desired: (1) to study which combinations of properties are key for an application, (2) to optimize performances, (3) to develop industrial applications if the production method is scalable. Independent control on heterogeneous catalysts' properties is challenging with the direct formation of NPs on supports: agglomeration and NP formation in pores lead to underutilization of the precious metal under catalytic operation. Our strategy is to use colloids to optimise independently several physical properties of the NPs. Yet in colloidal productions, surfactants are typically required and need to be removed in energy and time consuming steps, resulting in loss of catalytic performances due to sintering and poisoning.

A surfactant-free colloidal synthesis addressing the previous challenges is presented. Pt NPs are obtained at low temperature (< 80 °C) in alkaline mono-alcohols. The method is robust, reproducible, promisingly scalable and flexible (e.g. using microwaves, hot water bath, UV irradiation, flow systems). The mono-alcohol synthesis shows multiple benefits over alternative routes. It is interestingly sensitive to parameters screened in other approaches. The influence of solvents, time of synthesis and nature of base to achieve NP size in the range 1-6 nm and colloidal stability over several months, including in aqueous media, are detailed. The NPs are characterized by TEM, STEM, FTIR, SAXS, PDF, XAS, and electrochemical methods.

The energy, time and cost effective production of NPs in low boiling point solvents leads to improved catalytic performances compared to industrial benchmark for chemical production (butanone hydrogenation) and energy conversion (oxygen reduction).



Catalytic activity of benchmark and homemade Pt catalysts for butanone hydrogenation. A same mass of Pt is used for each experiments.

COLL 504

Cation exchange as a route to quantum dot synthesis: Are the daughter quantum dots inherently defective?

Chen Lin, Savannah E. Benjamin, Hailey D. Hall, Mackenzie L. Ary, Xyan A. Aguilar, Johnathan W. Campbell, Paul G. Van Patten, greg.vanpatten@mtsu.edu. Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee, United States

Cation exchange (CE) reactions, including two-step cation exchange, has emerged as a promising synthetic approach to new types of metal chalcogenide nanocrystals and heterostructures. An important question about CE as a synthetic approach concerns the potential to produce high-quality, defect-free particles. This work addresses our recent studies on this question with emphasis on four primary areas of concern. The first area of concern is the compositional purity of the product. How feasible is it to remove and replace 100% of the cation that is being exchanged? How much of the initial cation remains as a contaminant in the product? The second area of concern is the size and shape distribution of the product. How well is morphology maintained in the product nanocrystals, and what are the limiting factors? The third area of concern relates to the introduction or exclusion of lattice defects such as stacking faults in the product nanocrystals. Are such defects more prevalent in the daughters than in the parent nanocrystals? Finally, the fourth question concerns the ability to achieve the excellent optical properties such as high luminescence quantum yield and narrow bandwidth that would typify high quality quantum dots prepared by direct synthesis. Results will be presented from II-VI quantum dot systems that have been prepared via CE and compared both with the parent particles and also with particles prepared by direct synthesis.

COLL 505

Photoinitiated growth of silver nanoparticles in solutions of organic acids

David P. Pullman¹, dpullman@mail.sdsu.edu, **Nobuyuki Yamamoto**², **Renee Leslie**¹, **Michael Keogh**¹. (1) *San Diego State University, San Diego, California, United States* (2) *Chemistry, San Diego State University, San Diego, California, United States*

Silver aggregates of varying size and shape are known to form when aqueous solutions of silver ions and organic acids are exposed to UV and visible light for extended periods, but the products and growth kinetics are often irreproducible from solution to solution. We have undertaken a detailed mechanistic study to identify the source of the variations, with the goal of developing a method to control the size dispersion and morphology of photoproduced nanoparticles. Our results show that trace levels of transition metal ions ($[M^{+n}] / [Ag^+] < 0.001$), particularly di- and tri-valent ions present for example in the starting reagents, play a dominant role in initiating the nanoparticle growth. Some metal-organic complexes formed between these ions and the acids can absorb light through a charge transfer transition, resulting in the production of reduced ions as well as free radicals, both of which can serve to reduce Ag^+ . Once Ag^0 is produced, the growth of silver nanoparticles proceeds rapidly. By using ultrapure reagents and introducing known amounts of the transition metal ions, the size dispersion and shape of the nanoparticles can be controlled. The generality of this mechanism, including the production of other types of nanoparticles, and its possible application to environmental processes will be discussed.

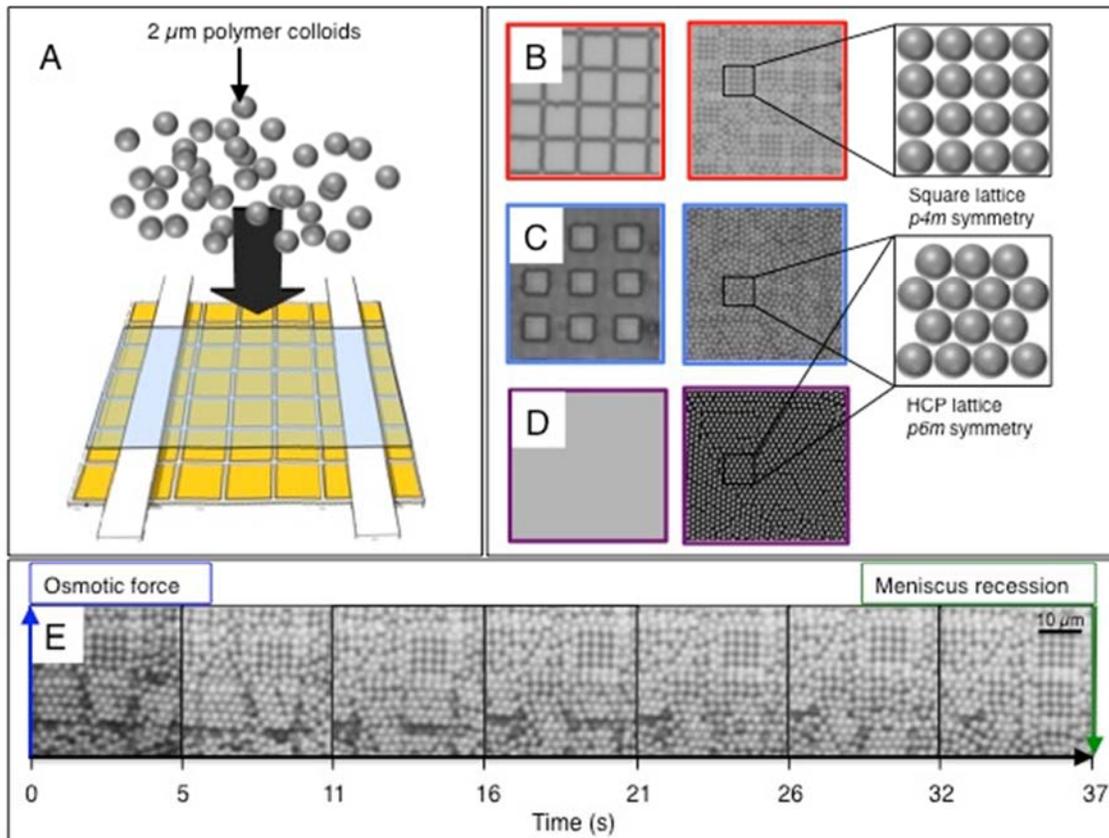
COLL 506

Controlled packing and phase transitions via templated evaporative colloidal assembly

Cicely Shillingford^{1,2}, cicely.shillingford@gmail.com, **Veronica Grebe**^{1,2}, **Angus McMullen**^{3,4}, **Marcus Weck**^{5,2}. (1) *Chemistry, New York University, New York, New York, United States* (2) *Molecular Design Institute, New York, New York, United States* (3) *Department of Physics, New York University, New York, New York, United States* (4) *Center for Soft Matter Physics, New York, New York, United States* (5) *New York University, New York, New York, United States*

Colloidal assembly is one of the most sophisticated analogues to nature's hierarchical assembly, in which simple building blocks are used to fabricate crystalline functional materials with nano/microscale features. We describe the fabrication of polycrystalline colloidal films using evaporative assembly and confinement within square wells in which both the height (h) and spacing (s_p) of the boundary are much less than the diameter of the particle. At high volume fractions, the colloids experience a long-range osmotic force that propagates upward from the evaporation front and induces a phase shift from hexagonal closed packed (HCP) to tetragonal packed regions (TP); in contrast to the open-to-closed packed transitions typically observed for colloidal self-assembly in

suspension or onto non-pattered substrates. The shifts in packing density over time and as affected by geometric templates with boundaries of various h and s_p values are quantified using a connectivity matrix. We investigate the optimal osmotic force necessary to produce square packed lattices and provide insight on controlling colloidal crystal order using geometric confinement, which will ultimately be extended to analyze evaporative packing of shape anisotropic particles into open lattices.



A) Experimental setup: $2\mu\text{m}$ 3-(trimethoxysilyl)propyl methacrylate (TPM) colloids were injected into a flow cell containing a patterned substrate and the liquid was evaporated. B) Regions of tetragonal packed colloids result from evaporation onto templates where both the height (h) and spacing (s_p) of the wells are less than the particle diameter (d). Hexagonal closed-packed regions are observed when the spacing between square patterns is large C), as seen also in the negative control D). E) The osmotic force caused by the meniscus recession produces a phase transition from HCP to TP; this originates from TP nuclei generated from geometric confinement by the shallow square fences.

COLL 507

Nanopore observations of pH dependent fluctuations in mercaptobenzoic-capped gold nanoclusters

*Bobby Cox, Patrick Woodworth, Massimo Bertino, **Joseph Reiner**, jereiner@vcu.edu. Physics, Virginia Commonwealth University, Richmond, Virginia, United States*

Metallic nanoclusters are highly stable particles made from a small number of atoms (<50). Utilizing these nanoparticles in aqueous environments requires the addition of water-soluble ligands. Previous work in our lab focused on glutathione-capped gold clusters and their role in enhanced nanopore detection of polymers and peptides. In an attempt to expand the gold metallic cluster toolbox for nanopore sensing, we have explored other water-soluble ligands with the most recent focus on mercaptobenzoic acids (MBA). This presentation will describe our results that show a strong relationship between solution pH and ligand-induced nanopore current fluctuations. Analysis of these fluctuations shows quantized current states indicative of protonation-deprotonation kinetics and suggests a new approach to characterizing nanoclusters at the single cluster limit.

COLL 508

Crystal face identification by Raman spectroscopy and application to the epitaxial growth of acetaminophen

***Tharanga K. Wijethunga**, tharanga@mit.edu, Jelena Stojaković, Michael Bellucci, Xingyu Chen, Allan S. Myerson, Bernhardt Trout. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States*

Crystal morphology or crystal habit is one of the key crystallographic characteristics and can directly influence the properties of the crystalline material. Thus, it is important to control these features of crystals in order to avoid the unpredictable property alterations in the process of crystallization. Face indexing is one of the techniques used to get important information regarding a crystal's morphology. Currently, the only developed method to experimentally determine crystal faces is the indexing by single crystal X-ray diffraction (SCXRD). However, limitations such as the requirement of high quality and specific size crystals, special instrumentation, and expert knowledge hinder the use of SCXRD with most crystals obtained under actual crystallization conditions. To circumvent this, we have developed a general method for the identification of the crystal faces using Raman spectroscopy. This method is based on the Raman polarizability, which affects the intensity of Raman peaks in the spectra depending on the crystal symmetry and the orientation of the sample. The procedure follows the steps of building a Raman library, validating the library against SCXRD data and the application of the library to the respective crystal systems. The developed method was successfully applied to three different epitaxial systems with a range of crystal sizes and quality. Acetaminophen (APAP) was grown as an overlayer crystal on D-mannitol (MAN), D-galactose (GAL), and xylitol (XYL) substrates. Six different face families for APAP and four different face families for each substrate were compiled into a Raman spectral library, which was then successfully used to identify the crystal faces of epitaxial pairs obtained under various experimental conditions.

COLL 509

Kinetics of self-assembly: Experimental probes of noble metal nanoparticle formation

Murielle Watzky, *murielle.watzky@unco.edu*, Haley Sandoe, Austin Ethridge. Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, Colorado, United States

Silver nanoparticles now stand amongst the most extensively produced nanomaterials, in large part due to their known wide-spectrum antimicrobial properties. Noble metal nanoparticles have also been integrated towards the development of a broad range of biosensing applications, which utilize their strong optical sensitivity via surface plasmon resonance. Here, silver nanoparticles and gold-silver core-shell nanoparticles were prepared via well-established modifications of the Turkevich method. Kinetics of silver nanoparticle formation, silver shell formation, and/or silver ion consumption were measured both by indirect (surface plasmon resonance/UV-visible spectroscopy) and other, more direct methods (ion selective potentiometry and atomic absorption spectroscopy). The resulting kinetic curves were fitted to the Finke-Watzky 2-step model of slow, continuous nucleation ($A \rightarrow B$, rate constant k_1) and fast, autocatalytic growth ($A + B \rightarrow 2B$, rate constant k_2); average rate constants for nucleation and growth were extracted from the curvefits. Numerical values of the nucleation and growth rate constants measured by indirect (surface plasmon resonance) versus other, more direct methods were analyzed. The advantages and limitations of each type of experimental probe were examined and assessed.

COLL 510

Engineering the assembly of semiconducting two-dimensional materials prepared by molecular tweezer chemical exfoliation technique

Mahmoud A. Mahmoud^{1,3}, *mahmoud.abdelwahed@UTSA.edu*, **Mohammad Abdul-Moqueet**², *mohammad.abdul-moqueet@my.utsa.edu*. (1) Chemical Engineering, the University of Texas at San Antonio, San Antonio, Texas, United States (2) Physics and Astronomy, the University of Texas at San Antonio, San Antonio, Texas, United States (3) Chemistry, the University of Texas at San Antonio, San Antonio, Texas, United States

The semiconducting two-dimensional materials (2DM) functionalized with polymers are prepared by a new technique based on the exfoliation of thin layer flakes from the surface of the crystals using molecular polymer tweezers. The forces generated by the vibration of polymer tweezers, which are induced by sonication, are used to cleave off 2DM flakes from the surface of the crystal. The polymer bonds to the surface of the crystal via a covalent bond, which is stronger than the Van der Waals interaction between the 2DM layers. The prepared polymers functionalized to the surface of the 2DM are able to semi-crystallize; thus making it possible to control the 2D and 3D

assembly of the 2DM on the surface of different substrates by LB technique. The fundamental theory behind the changing of the structure of the assembly for 2DM is discussed.

COLL 511

Mechanically robust thin films coatings from functionalized silica nanoparticles

Melike Barak¹, mbarak@sabanciuniv.edu, **Fevzi C. Cebeci^{1,2}**, **E B. Sevinis Ozbulut¹**. (1) *Faculty of Engineering & Natural Sciences, Sabanci University, Istanbul, Tuzla, Turkey* (2) *Nanotechnology Research & Application Center, Istanbul, Tuzla, Turkey*

Layer by Layer (LbL) assembly is a well-known approach to create coatings of water dispersible molecules and materials. LbL offers exceptional advantages like conformal coatings with controlled structure and composition. Essential principle of LbL method is assembly of oppositely charged materials sequentially by electrostatic interactions. These interactions may yield weaker mechanical properties, such disadvantages could be eliminated by introducing covalent bonding between functional groups of oppositely charged materials.

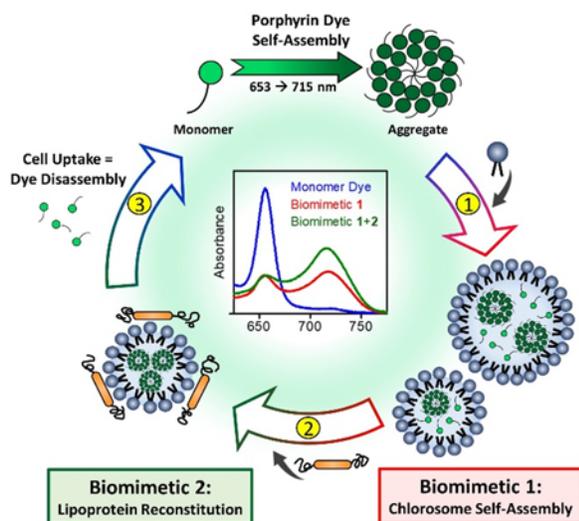
In this study, LbL assembled thin film coatings of functionalized silica nanoparticles showing favorable mechanical robustness by crosslinking are demonstrated. Monodisperse silica nanoparticles are synthesized by hydrolysis and condensation of tetraethyl orthosilicate inside surfactant/cyclohexane/ammonia media to obtain controlled nanoparticle size by microemulsion method. Amino acid, amino, and poly(ethylene glycol)-terminated alkoxy silanes that aimed to provide positive and negative surface charges were covalently bonded to the silica nanoparticles. Dynamic light scattering is employed to analyze surface charge distribution, chemical composition and thermal response of functionalized silica nanoparticles are characterized by Fourier-transform infrared spectroscopy and thermogravimetric analysis respectively. Charged nanoparticles and polyelectrolytes are deposited on glass and silicon wafer substrates to create thin film coatings by LbL assembly. The thickness, roughness and optical properties of thin films are measured by ellipsometry, surface profiler and atomic force microscopy. Transmission and reflectance properties are investigated by ultraviolet visible spectrophotometer. The obtained results indicated that chemically crosslinked silica nanoparticle containing thin films exhibit better mechanical properties that make them useful for demanding applications.

COLL 512

Multi-pronged biomimetic approach to create optically tunable nanoparticles

Kara M. Harmatys^{1,3}, kharmaty@alumni.nd.edu, **Juan Chen¹**, **Danielle M. Charron^{1,2}**, **Christina M. MacLaughlin¹**, **Gang Zheng^{1,3}**. (1) *University Health Network, Princess Margaret Cancer Centre, Toronto, Ontario, Canada* (2) *Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada* (3) *Medical Biophysics, University of Toronto, Toronto, Ontario, Canada*

Inspired by nature, biomimetics can be exploited for their structural and/or functional properties for chemistry, biology, engineering and medicine. Current systems often use a single biomimetic structure, which can be challenging to reconstruct given the complexity existing in most natural systems. Therefore, multi-pronged efforts may resolve these complexities when single biomimetic systems are insufficient. In our quest for interesting nanostructure-driven properties, we engineered a dual-biomimetic system contained within a single nanoagent to recapitulate the function of a complex natural photosynthetic system for bioimaging applications. The first component chosen mimics the efficient light-harvesting organelles found in green photosynthetic bacteria, chlorosomes, which have unique dye supramolecular assemblies and tunable photonic properties. To accommodate these hydrophobic assemblies for *in vivo* applications, we incorporated a second component to mimic high-density lipoprotein, which was designed to stabilize the intact dye-assembly and impart favorable *in vivo* behavior. For chlorosome reconstruction, we synthesized a series of chlorin derivatives where a 3¹-OH substitution and zinc metal insertion enabled intermolecular metal-oxygen coordination and a conjugated lipophilic oleylamide anchored the chlorin within the lipoprotein interior for complete ordered dye packing. Intact nanoparticles reveal the chlorin ordered assembly absorption (715 nm) red-shifts from its monomer (654 nm), which quenches porphyrin fluorescence, enabling *in vivo* photoacoustic imaging (PAI). When the nanostructure is disrupted in tumor cells, porphyrin properties are restored for low-background fluorescence imaging (FI), enabling tunable bioimaging (PAI/FI). The successful demonstration of this multi-pronged biomimetic approach opens the door for reconstruction of complex natural systems for biomedical applications.



COLL 513

InP-based alloy quantum dots and their compositional effects on thermal/chemical stability

Richard P. Brown¹, rbrown6@umbc.edu, Zeev Rosenzweig². (1) Chemistry, University of Maryland Baltimore County, Bel Air, Maryland, United States (2) Chemistry and

Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland, United States

Over the past few decades, luminescent semiconductor quantum dots (QDs) have emerged as promising materials for light emitting/absorbing applications, including but not limited to bioimaging, light emitting diodes, displays and photovoltaics. These applications raise the possibility of broad commercial implementation (LEDs and photovoltaics) and intimate biological association (bioimaging). The cadmium chalcogenides such as CdSe, CdS and CdTe QDs have been at the forefront of QD design and performance. Environmental and human health concerns over the use of highly toxic cadmium have driven the field to find cadmium-free alternative materials that retain their superb functions of cadmium-containing QDs while minimizing their environmental and human health impact. InP and InP/ZnS core/shell QDs have emerged as a potential alternative to cadmium-containing QDs. The presentation will introduce a unique synthesis approach to yield InP/ZnS QDs with high emission quantum yield and narrow emission peaks across a broad range of emission peak wavelengths. The presentation will also describe the impact of QD composition on the optical properties of InP(x)/ZnS alloys/multilayer core/shell QDs and their chemical stability towards oxidation and dissolution in organic solvents and aqueous media.

COLL 514

Colloidal nanoparticles directly observed by multi-dimensional liquid phase TEM

*Byung Hyo Kim^{1,2}, Junyoung Heo^{1,2}, Sungin Kim^{1,2}, Joodeok Kim^{1,2}, Donghoon Lee^{1,2}, **Jungwon Park^{1,2}**, jungwonpark@snu.ac.kr. (1) School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of) (2) Nanoparticle Research Center, Institute for Basic Science, Seoul, Korea (the Republic of)*

Liquid cell TEM (LTEM) has been introduced recently for *in-situ* study of chemical reactions occurring in liquid. Liquid cells allow an opportunity to utilize high spatial and temporal resolution of TEM in studying reactions of colloidal nanoparticles. Achieving sub-nm spatial resolution by adjusting the thicknesses of window materials and the encapsulated liquid, important steps in growth trajectories of different types of nanoparticles have been directly observed at high-resolution of TEM. Along with computational analysis, we also study growth trajectories of ensemble number of nanoparticles. We also observe the diffraction patterns from individual nanoparticles as they rotate in the liquid cell, and ultimately, we are able to align and invert those images to obtain the 3D atomic structure of individual particles freely moving in liquid. Obtained 3D density maps unveil structural features of nanoparticles that have been either underestimated or unattainable in conventional analysis. We present our efforts to augment a combination of above-mentioned analytical tools in directly observing chemical reactions of nanoparticles in reactive environments.

COLL 515

High-resolution single molecule force spectroscopy using carbon nanotubes in an optical tweezer

Daniel J. Jackson¹, jdanson@bu.edu, **Maria Kamenetska**². (1) Chemistry, Boston University, Allston, Massachusetts, United States (2) Chemistry and Physics, Boston University, Boston, Massachusetts, United States

As we seek to gain a mechanistic understanding of phenomena at the nanoscale, we require approaches to probe the single molecule regime. Few single molecule techniques exist to enable chemists to observe solution phase dynamics at the single molecule level. Here we extend on a recently published universal optical trapping platform for single molecule force spectroscopy in both aqueous and organic solvents. We propose that carbon nanotubes (CNTs), which have a high persistence length, can act as stiff linkers in optical trapping experiments in a variety of solvents. For biophysical measurements, stiffer linkers made from DNA origami structures have been shown to increase signal-to-noise in single molecule force spectroscopy compared to measurements using double stranded DNA or synthetic organic polymers. We argue that the use of CNTs, which are easily functionalized for click-chemistry binding in an optical tweezer, will open the door to the study of solution phase chemistry at the single molecule level.

COLL 516

Architecting corrosion-resistant alloys through nanoscale morphology

Alison Smith¹, alisonsmith4321@gmail.com, **Yunusa Balogun**¹, **Xingchen Ye**². (1) Global Deterrence & Defense, NAVSEA Crane, Crane, Indiana, United States (2) Chemistry, Indiana University, Bloomington, Indiana, United States

Globally, addressing corrosion issues throughout our infrastructures costs upwards of \$2.5T annually. As such, there is a need for materials which are robust in operational environments. Traditional corrosion mitigation approaches are largely dominated by anodic/cathodic protection and coating designs. However, recent reports of the shape evolution of anisotropic metallic nanocrystals (NCs) during dissolution suggest that a new morphology-driven approach may be added to this corrosion mitigation toolbox. These studies tracked NC morphology changes, using *in situ* transmission electron microscopy (TEM), and revealed that some colloidal NC shapes are short-lived while others are much longer lived. While the implications of these studies focused on the fundamental insight into NC morphology-stability relationships, we expand those implications to include new strategies to reduce corrosion susceptibility. For example, nanostructures that are resistant to dissolution in highly oxidizing environments may inform the design and selection of finishing processes that will yield corrosion-resistant materials. Currently, there is a lack of morphology-lifetime correlation in corrosive environments for alloy NCs in which selective oxidation becomes a critical factor. Here,

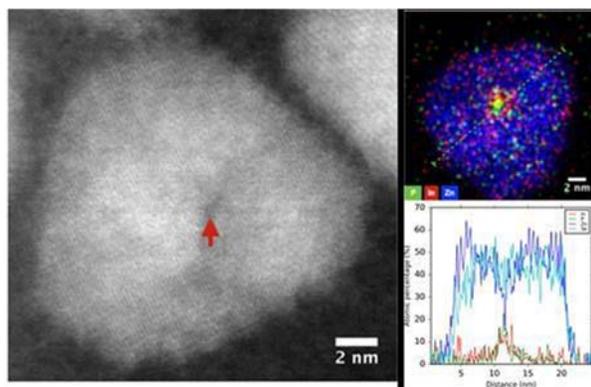
we present a mechanistic understanding of nanoscale structural evolution, in corrosive environments, for a model alloy system utilizing *in situ* TEM. This mechanistic understanding drove the development of morphology-based design rules to inform the selection of materials that are resilient throughout their lifecycle.

COLL 517

Informing nanocrystal synthesis *via* correlated atomic structure and single nanocrystal photophysics

James R. McBride, james.r.mcbride@vanderbilt.edu, **Kemar Reid**, **Sandra J. Rosenthal**. *Chemistry, Vanderbilt University, Nashville, Tennessee, United States*

Much like NMR for organic chemists, conventional high resolution transmission electron microscopy (HRTEM) has been one of the primary tools for determining the structure of colloidal quantum dots. Analogous to synthetic impurities, even the best colloidal nanocrystal syntheses yield a distribution of structures which collectively produce the observed ensemble properties. Only by iterative approaches are the nanostructures ultimately optimized. In order to accelerate the development of emergent nanocrystal systems, a correlation method is needed that quickly identifies the particular structural motifs that yield the desired photophysical properties. Time correlated single photon counting spectroscopy coupled with fluorescence microscopy is a powerful tool that reveals the complex photophysics of colloidal quantum dots. Although allowing one to individually interrogate nanocrystals, their single particle fluorescence behavior is often linked to an ideal structure derived from separately obtained HRTEM. Dark particles will go completely undetected, dim particles may be overlooked while small aggregates can appear spectroscopically as a single particle. To address these concerns, we've developed an intuitive and reproducible method to correlate the atomic and chemical structure of individual colloidal nanocrystals with the same particle's fluorescence dynamics. With this correlation technique it is possible to identify sub-populations of structures that exhibit the desired photophysics and then use that knowledge to direct chemistry to produce quantum dots with specifically chosen optical behavior. HRSTEM, advanced STEM-EDS and initial correlation results will be presented for thick shelled InP/ZnSe colloidal quantum dots that exhibit suppressed blinking. Interesting defects were observed in the HRSTEM images while the STEM-EDS maps confirm a substantial inclusion of indium in the shell.



HRSTEM and STEM-EDS of thick shelled InP/ZnSe core/shell nanocrystal

COLL 518

Single-crystal electrochemistry reveals why nanowires grow

Benjamin J. Wiley, bjw24@duke.edu. *Chemistry, Duke University, Hillsborough, North Carolina, United States*

Metal nanowires are essentially sticks of metal with diameters usually in the tens of nanometers and lengths in the tens of micrometers, giving them aspect ratios around 100-1000. Despite the fact that an increasing number of applications rely on nanowires grown in solution-phase syntheses, the mechanism by which nanowires grow to have a high aspect ratio has largely remained a mystery. This presentation will show how measurements with single-crystal electrodes can be used to reveal the facet-selective chemistry that drives anisotropic growth of metal nanowires. Solution-phase synthesis generally involves heating a solution containing a metal salt, a reducing agent, and a shape-directing organic additive (usually referred to as a capping agent) that is necessary for anisotropic growth. Pentagonally-twinned nanowires of Cu, Ag, and Au have (100) facets on their sides and (111) facets on their ends. Researchers have hypothesized that organic capping agents direct anisotropic growth by selectively inhibiting atomic addition to the (100) facets. This presentation will show this hypothesis is wrong for two different syntheses of Cu nanowires. For a Cu nanowire synthesis in which ethylenediamine serves as the capping agent, ethylenediamine acts as a facet-selective promoter of Cu nanowire growth by keeping the Cu(111) surface relatively free of surface oxidation in the highly basic growth solution (>12 M NaOH). This resulted in a ~6 minute window during which hydrazine reduced Cu ions onto Cu(111) while reducing surface oxides on Cu(100). The ~6-minute period of facet-selective Cu deposition closely matched the time scale over which Cu nanowires switch from longitudinal to lateral growth in the actual nanowire growth solution. In another synthesis in which hexadecylamine is a capping agent, electrochemical measurements on Cu(111) and Cu(100) surfaces show that, in contrast to previous hypotheses, hexadecylamine does not selectively passivate Cu(100); it passivates both facets equally. However, the introduction of Cl⁻ in a narrow range of concentrations selectively disrupts the

alkylamine monolayer on Cu(111), causing Cu to preferentially deposit onto (111) facets on the ends of the nanowires.

COLL 519

***In-situ* measuring the electronic structure of nanocrystal thin films using energy-resolved electrochemical impedance spectroscopy**

Sebastian Volk¹, svolk@ethz.ch, Nuri Yazdani¹, Olesya Yarema¹, Maksym Yarema¹, Vanessa Wood². (1) ETH Zurich, Zurich, Switzerland (2) Information Technology and Electrical Engineering, ETH Zurich, Zurich, Switzerland

Use of nanocrystal thin films as active layers in optoelectronic devices requires tailoring of their electronic band structure, often through graded and heterojunction structures. Here, we demonstrate energy-resolved electrochemical impedance spectroscopy (ER-EIS) and open-circuit voltage measurements as a method to quantify electronic structure and Fermi-level position in nanocrystal (NC) thin films. Unlike vacuum-based techniques for quantifying electronic structure, these electrochemical based techniques are well-suited for nanocrystal-based thin films as they allow for *in-situ* assessment of electronic structure during the solution-based fabrication of the thin film. Using well-studied lead sulfide nanocrystals as an example, we probe the energy position and number density of defect or dopant states as well as the modification of energy levels in nanocrystal solids that results through the exchange of surface ligands. These sensitive and fast methods to measure the electronic structure of nanostructured thin films under fabrication conditions provide insights into existing device operation and paths for further optimization in optoelectronic devices.

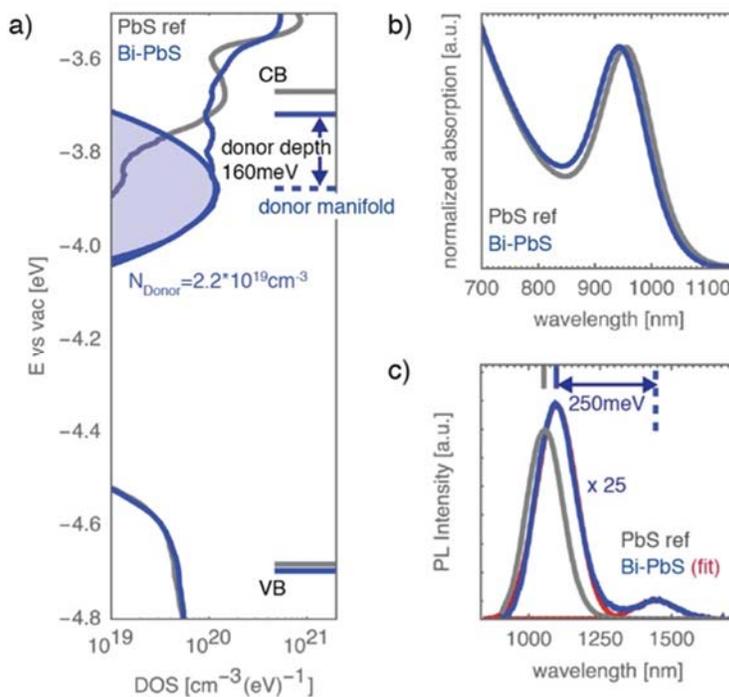


Figure 1. Observation of nanocrystal doping. a) The ER-EIS derived DOS for post-synthesis Bi-doped nanocrystal (NC) thin films are compared to undoped reference films. The Bi-doping introduces a donor manifold at a depth of 160 meV below the conduction band onset with a total number density of $2.2 \times 10^{19} \text{ cm}^{-3}$, translating into 2-3 donor states per NC. b) Optical absorption of the thin films shows a 17 meV redshift of the 1st exciton feature. c) Photoluminescence main peak of the Bi-doped PbS NCs decreases by a factor of 25 and a small signal feature at higher wavelengths emerges that is linked to the donor state to valence band transition.

COLL 520

Submolecular resolution spectroscopic imaging for photoactive molecules and assemblies

Shenkai Wang^{1,2}, shenkaiwang@ucla.edu, **Naihao Chiang**^{1,2}, **Natcha Wattanatorn**^{1,2}, **Paul S. Weiss**^{1,2}. (1) Chemistry and Biochemistry, UCLA, Los Angeles, California, United States (2) MC 722710, California NanoSystems Inst. UCLA, Los Angeles, California, United States

The photoconversion of sunlight directly to electricity is essential for meeting future energy needs. Organic photovoltaic devices consisting of small-molecule donor-acceptor heterojunctions show great promise for photoconversion due to their ease of manufacture, their synthetic variability, and their cost effectiveness. Understanding electron transfer at the molecular level is critical for the rational design and performance optimization of organic optoelectronics and photovoltaics. We use our custom-built laser-assisted scanning tunneling microscope (photon STM) to measure photo-induced charge generation and separation in *p-n* junctions at the submolecular level under ambient conditions. Photoactive molecules were deposited on sapphire-prism-supported Au{111} substrates to form ordered self-assembled monolayers or were isolated in defects within dodecanethiol self-assembled monolayers. The surfaces were characterized by scanning tunneling microscopy and lasers modulated by a chopper wheel were introduced into the tunneling junction *via* total internal reflection. The chopper wheel creates a reference frequency input to a lock-in amplifier (LIA) for phase-sensitive detection, so that light-triggered changes in the tunneling current can be recorded and spatially resolved with submolecular resolution. This spectroscopic imaging technique has the potential to elucidate photo-induced carrier dynamics that are inaccessible at ensemble levels and that can be used to direct the rational design and optimization of molecular *p-n* junctions.

COLL 521

Field effect transparency of 2D materials: A multiscale analysis

Tian Tian¹, tian.tian@chem.ethz.ch, **Peter Rice**², **Elton J. Santos**², **Chih-Jen Shih**¹. (1) D-CHAB, ETH Zürich, Zürich, Switzerland (2) School of Mathematics and Physics, Queen's University Belfast, Belfast, United Kingdom

The field effect has been widely involved in gate-tunable two-dimensional (2D) materials and van der Waals heterostructures (vdWH) devices for tuning the transport or optoelectronic characteristics. Recent studies have attributed the observed gate-tunable characteristics to the change of the energy level in the first 2D layer adjacent to the dielectrics, while the penetration of the field is often ignored or over-simplified. The one- or few-atomic thickness and low density of states of 2D materials make them transparent to electric displacement field compared with their bulk counterparts. Here, taking graphene as an example, we present a multiscale theoretical approach that combines first-principles electronic structure calculations and the Poisson-Boltzmann equation methods to model penetration of electric displacement field in a metal-oxide-graphene-semiconductor (MOGS) quantum capacitor (QC), including quantifying the degree of field effect transparency for the two-dimensional electron gas. We find that the space charge density in the semiconductor layer can be modulated by the displacement field in a nonlinear manner, forming an accumulation or inversion layer at the semiconductor/graphene interface. We further show that the degree of field effect transparency is determined by the combined effect of graphene quantum capacitance and the semiconductor differential capacitance, which allows us to predict the ranking for a variety of monolayer 2D materials according to their transparency to an electric displacement field as follows: graphene > silicene > germanene > WS₂ > WTe₂ > WSe₂ > MoS₂ > phosphorene > MoSe₂ > MoTe₂, when the majority carrier is electron. Our findings provide a systematic understanding of the field effect transparency through a 2D material, and reveal a general picture of operation modes and design rules for the 2D-material-based devices and heterostructures.

COLL 522

Contact resistance of carbon nanotubes in vertically aligned carbon nanotube forest

Meng Li², mli@ethz.ch, Ning Yang¹, Vanessa Wood², Hyung Gyu Park¹. (1) Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland (2) Information Technology and Electrical Engineering, ETH Zurich, Zurich, Switzerland

Despite technological significance and extensive investigations of electrical and electrochemical properties of carbon nanotubes (CNTs), an understanding of the origin of their high contact resistance remains elusive partly due to difficult characterization. Here, we demonstrate a method to probe the contact resistance of CNTs over a large area in their vertically aligned (VA) configuration. With a tube density extracted from the VACNT growth data, end-contact and side-contact resistances of individual CNT can be determined by two-probe electrical current-voltage measurement and electrochemical impedance spectroscopy, respectively (**Figure 1**). We find that the energy gap between CNT and contact material plays a vital role. In end-contact mode, metal with stronger affinity to the CNT tip and less spacing for electron tunneling displays a lower resistance. Between CNT and semiconducting oxide in a side-contact configuration, a Schottky barrier governs the electron transport at the interface.

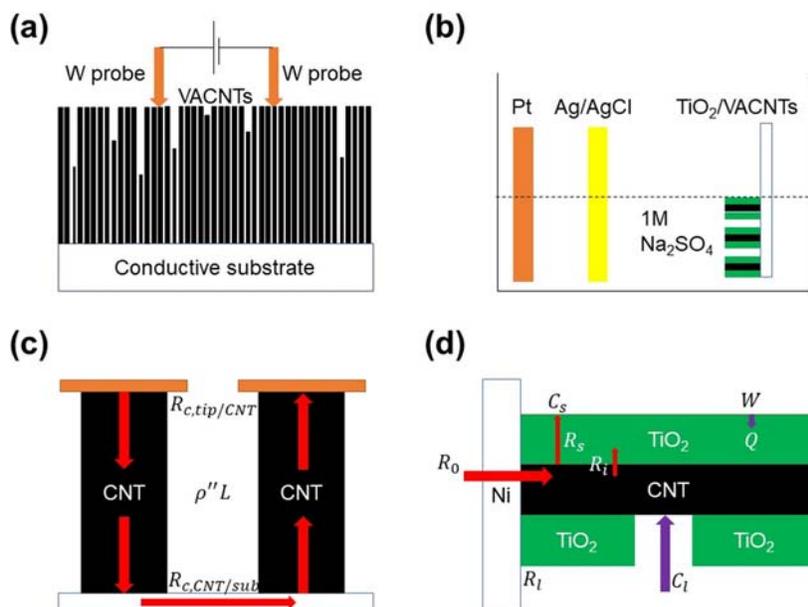


Figure 1. Schematic setup of (a) end-contact and (b) side-contact measurements. (c) and (d) are the magnification views of an individual CNT, displaying the electrical (in red) and ionic (in purple) impedances in various locations.

COLL 523

Semiconductor nanoplatelets: A new class of ultrabright and biocompatible probes for biological applications

Djamila Kechkeche, djamila.kechkeche@nexdot.fr. Physique et chimie des matériaux, Pierre et Marie Curie, Paris, France

Fluorescent semiconductor nanoplatelets (NPLs) are a new generation of fluorescent labels. NPLs are colloidal two-dimensional materials that exhibit several unique optical properties including high brilliance, high fluorescent photostability, high extinction coefficients, broad excitation and narrow emission spectra. However, NPLs are synthesized in organic solvents and coated with hydrophobic ligands that render them insoluble in water. A current challenge is to stabilize NPLs in aqueous media compatible with biological environments. Here we propose, for the first time, a ligand exchange method to disperse different colors of NPLs in water while maintaining good optical properties. NPLs were transferred in aqueous media by ligand exchange with a small monodentate hydrophilic ligand, namely 3-mercaptopropionic acid. Monothiol anchoring to semiconductors are prone to photo-oxidation and can desorb in dilute solutions. In order to circumvent these issues, we developed a multidentate polymeric ligand that binds to the surface of NPLs. NPLs showed then exceptional long term colloidal stability regardless of several medium conditions, such as a broad pH range from 5.3 to 9.5, high ionic strength buffer (200 mM NaCl), and storage at nanomolar concentration (10

nM). After ligand exchange, at least 70% of NPLs quantum yield is conserved (from an initial 90% in organic media) and their fluorescence emission bandwidth remained narrow (around 25 nm full width at half maximum).

To demonstrate NPLs potential for biodetection, we functionalized them with different biological molecules through self-assembly strategies based on histidine-tagged biomolecules or by covalent bonds. We conjugated genetically engineered proteins that incorporated 15-unit long histidine tags, specifically protein A, mCherry and GFP, on the surface of NPLs with a bioconjugation yield efficiency of 95%. Afterwards, we immobilized anti-human CD3 antibody (Ab) on the surface of NPLs by using protein A as intermediate layer that specifically binds Ab. We also immobilized streptavidin (SAV) on the surface of NPLs by sulfhydryl-maleimide chemistry. NPLs-SAV conjugates were used to stain human lymphocytes through biotinylated Ab. We compared the staining index of these NPLs-SAV alongside popular fluorochromes like Phycoerythrin (PE) and Brilliant Violet 650™ (BV650™) using flow cytometry. We obtained a staining index of 39, 32 and 23 for NPLs, BV650™ and PE, respectively.

COLL 524

Fluorescent nanoparticle sensor for hormones based on a native microbial transcription factor

Chloe Grazon^{1,4}, cgrazon@bu.edu, *Thuy Nguyen*², *R C. Baer*³, *Uros Kuzmanovic*³, *Margaret Chern*², *Mingfu Chen*², *Marjon Zamani*², *Andy Fan*², *Xiaoman Zhang*³, *Sebastien Lecommandoux*⁴, *Catherine Klapperich*², *Allison M. Dennis*², *Mark W. Grinstaff*^{1,2}, *James Galagan*³. (1) Chemistry, Boston University, Brookline, Massachusetts, United States (2) Biomedical Engineering, Boston University, Boston, Massachusetts, United States (3) Biomedical Engineering and Microbiology, Boston University, Boston, Massachusetts, United States (4) LCPO-ENSCP, University of Bordeaux 1, Pessac, France

Connected devices that monitor human biology in real-time represent the next frontier in biosensors. Monitoring hormones is of significant interest as hormones play critical roles in multiple physiological processes including stress adaptation, blood pressure control, reproductive rhythms, and body odor. However, the real-time monitoring of hormones is challenging from a biology, chemistry, and engineering perspective. We are designing and developing a novel sensor for progesterone. Our approach combines microbial genomics and protein engineering, new polymer and nanoparticles compositions, and sensor design. The biosensor is composed of Quantum Dots (QDs) decorated with a hormone-sensitive transcription factor (TF) and a fluorescently-labelled DNA. Without the hormone, the DNA binds the TF and a fluorescence resonance energy transfer (FRET) signal is emitted between the QDs and the fluorescent DNA, while in the presence of progesterone, the DNA and TF separates and only one fluorescent signal from the QDs is emitted. Using such a simple but versatile system, nanomolar levels of progesterone are detected in solution.

COLL 525

Integrated multifunctional nanoplatform based on superparamagnetism and near-infrared to near-infrared photoluminescence for deep-tissue dual-mode imaging

Fan Yang¹, fan.yang@emt.inrs.ca, **Artiom Skripka**¹, **Antonio Benayas**^{1,2}, **Xianke Dong**³, **Sung Hwa Hong**⁴, **Fuqiang Ren**¹, **Jung Kwon Oh**⁴, **Xinyu Liu**³, **Fiorenzo Vetrone**¹, **Dongling Ma**¹. (1) EMT, Institut National de la Recherche Scientifique Énergie, Varennes, Quebec, Canada (2) Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal (3) University of Toronto, Toronto, Ontario, Canada (4) Department of Chemistry and Biochemistry, Concordia University, Montreal, Quebec, Canada

Dual-mode imaging, which combines optical and magnetic resonance (MR) imaging, as a diagnosis tool for cancer at early-stage has been shown to be particularly attractive because it will allow retrieving both macroscopic and subcellular information of bio-species, and thus leading to improved diagnostic accuracy. To this end, a variety of multifunctional multifunctional (superparamagnetic and photoluminescent) nanoparticles (NPs) have been specifically designed for dual-mode imaging. However, most of these hybrid NPs show shallow tissue penetration and low signal contrast in optical imaging due to the tissue-induced extinction and autofluorescence since their photoluminescent components based on organic dyes, upconversion nanoparticles (UCNPs) and quantum dots (QDs) are operated in the visible range. In this work, we prepare a biocompatible core/shell/shell sandwich structured $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NaYF}_4:\text{Nd}^{3+}$ nanoplatform possessing excellent superparamagnetic and near-infrared (excitation) to near-infrared (emission), i.e., NIR-to-NIR photoluminescence properties. This NIR-to-NIR feature enables deep-tissue penetrated optical imaging with high signal-to-noise ratio which was demonstrated by the *ex vivo* experiment of chicken samples with thickness of 13 mm. Meanwhile, owing to the superparamagnetic Fe_3O_4 core inside, this nanoplatform can be rapidly confined under an external magnetic field and exhibited a significant darkening effect in T_2 -weighted images in MR imaging. More importantly, the developed NPs are much less toxic than semiconductor QDs, which usually contain Pb and/or Cd. These results including excellent photostability, fast magnetic response, significant T_2 -contrast enhancement and negligible cytotoxicity suggest that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NaYF}_4:\text{Nd}^{3+}$ nanoplatform can be extremely suitable for use in high resolution, deep-tissue dual-mode (optical and magnetic resonance) imaging *in vivo* and magnetic-driven applications.

COLL 526

Antifouling zwitterionic quantum dot surface chemistry: Impact on intracellular diffusion

Nicolas Lequeux¹, nicolas.lequeux@espci.fr, **Thomas Pons**², **Maxime Dahan**³, **Elie Balloul**³, **Manon Debayle**⁴. (1) LPEM, ESPCI-Paris France, Paris, France (2) LPEM, ESPCI, Paris, France (3) Institut Curie, Paris, France (4) Chemistry, ESPCI, Paris, France

Minimizing protein corona formation around nanoparticles by using stealth polymer is a current strategy to limit non-specific cellular uptake and to increase blood circulation time. In addition, the antifouling property is a prerequisite for specific targeting and drug delivery. PEG coating is most commonly used for this purpose but zwitterionic surface chemistry appears as an interesting alternative. The wide range of possible variations of zwitterionic materials is clearly an advantage compared to PEG but in return, the impact of the molecular design on protein-adsorption properties must be optimized. Here, we present some results about interactions between polyzwitterionic coated quantum dots and albumin or whole serum. Sulfobetaine, phosphorylcholine and carboxybetaine based polymers have been synthesized by RAFT. A terminal vinylimidazole block was added at the end of the polyzwitterion to ensure anchoring at the quantum dots surface. Hard protein corona formation was quantified after ultracentrifugation by fluorescamine assay. Fluorescence Correlation Spectroscopy (FCS) was used to characterize dynamic interactions between proteins and QDs directly.

We found that sulfobetaine based polymer is able to totally prevent hard and soft corona formation with BSA and proteins of serum around nanoparticles making this polymer ideal for antifouling applications. The phosphorylcholine and carboxybetaine ligands are less efficient and induce formation of few aggregates in serum. Intracellular trajectories of individual QD injected into Hela cells have been analyzed. The high diffusion coefficient ($D_{60\text{ms}} \sim 0.8 \text{ } \mu\text{m}^2\text{s}^{-1}$) and the purely Brownian motion point to the remarkable cytoplasmic inertness of these zwitterionic coated nanoparticles. This enables in turn efficient intracellular targeting in live cells.

Finally, we will discuss the impact of the modification of globally neutral polyzwitterions by the addition of some negatively or positively charged monomers on protein adsorption and intracellular diffusion.

COLL 527

Probing bio-nano interactions with colloidal poly(ethylene glycol) particles

Jiwei Cui, jwcui@sdu.edu.cn. Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education, Shandong University, Jinan, China

Successful accumulation of drugs specifically at diseased sites is mainly limited by biological barriers to drug transport, especially the nonspecific uptake of drug carriers in mononuclear phagocyte system (MPS). Hence, it is critical to develop drug delivery systems that can specifically bind to diseased cells, while avoiding interactions with normal, healthy cells. This presentation will demonstrate the engineering of polymer particles composed with poly(ethylene glycol) (PEG) itself using a mesoporous silica (MS) templating method, and will show the cell association and biodistribution of these particles, PEG particle deformation in a microcapillary model, as well as cell targeting of PEG particles modified with cyclic peptide targeting molecules.

PEG particles composed with large molecular weight of PEG and prepared from smaller MS templates result in longer circulation time and can avoid non-specific accumulation of PEG particles in spleen and liver. In addition, the deformability behavior of PEG particles can be tuned to be similar to that of human red blood cells via varying the

particle cross-linking density, which could avoid the filtration effect in vivo and therefore increase the circulation time of PEG particles. Surface modification of PEG particles with targeting molecules (e.g., cyclic RGD or antibody) can improve the specific cell targeting while keeping the stealth property of PEG particles. The optimization of PEG particle engineering to overcome the MPS biological barrier and show promising tumor targeting in mouse studies is examined by tuning PEG molecular weight, particle size, particle stiffness, and targeting molecule density, which highlights the influence of unique aspects of polymer particles on biological interactions. The reported PEG particles represent a new class of polymer carriers with potential biomedical applications.

COLL 528

Life and death in a bacterial biofilm under antibiotic attack characterized by fluorescence and atomic force microscopy

Catherine B. Volle¹, cvolle@cottey.edu, Helen Greer¹, Kanesha Overton¹, Megan Nunez², Megan A. Ferguson³, Eileen M. Spain⁴. (1) Biology, Cottey College, Nevada, Missouri, United States (2) Dept of Chemistry, Wellesley College, Wellesley, Massachusetts, United States (3) SUNY New Paltz, New Paltz, New York, United States (4) Dept. of Chemistry, M-5, Occidental College, Los Angeles, California, United States

With the increase in bacteria developing resistance to traditional antibiotics, there is a pressing need for new antibiotic compounds. Researchers are currently exploring the use of antimicrobial peptides as a new class of antibiotic drugs. Antimicrobial peptides are typically small and occur naturally as components of many immune systems. These peptides kill bacteria in one of two mechanisms. In the first mechanism, multiple peptide subunits join together to form pores in the bacterial membranes. In the second, the peptide crosses the membrane and binds to some molecule in the cell, preventing its action. Magainin II, first isolated from the skin of the African clawed toe frog *Xenopus leavis*, is a classic example of a pore-forming peptide and has been investigated in lipid micelles, bacterial spheroplasts, and various bacteria. However, much of the research on magainin II and other antimicrobial peptides has focused on free-swimming, planktonic bacteria, yet many bacteria live not as planktonic cells, but in an organized community called a biofilm. Due to their complex architecture and excreted exopolymeric substances (EPS), cells in the biofilm are notoriously hard to kill. Thus it is essential to evaluate the effectiveness and mechanism of action of any new classes of antibiotics on both planktonic and biofilm cells. Here we use fluorescence microscopy and atomic force microscopy (AFM) to evaluate the changes that occur in both planktonic and biofilm *Escherichia coli* cells when exposed to this antimicrobial peptide in native conditions. Notably, using AFM we find distinct changes in both cell stiffness and the morphology of the outer membrane after treatment of both planktonic and biofilm cells, but we also observe that the EPS protects some cells in the biofilm.

COLL 529

Developing gold nanoparticles for inhibiting cancer metastasis

Yue Wu¹, janewuyue@gmail.com, Moustafa R. Ali², Mostafa A. El-Sayed³. (1) Chemistry, Georgia Institute of Technology, Atlanta, Georgia (2) Georgia Institute of Technology, Atlanta, Georgia, United States (3) Georgia Inst of Techlgy, Atlanta, Georgia, United States

Metastasis is responsible for most cancer-related deaths, but the current clinical treatments are not effective. Recently, gold nanoparticles (AuNPs) were discovered to inhibit cancer cell migration and prevent metastasis. Rationally designed AuNPs could greatly benefit their anti-migration property, and the molecular mechanisms need to be explored. In our study, two types of gold nanoparticles have been developed in order to inhibit cancer cell migration and invasion: **1.1. Nuclear Membrane-Targeted Gold Nanoparticles.** Since nuclear stiffness of the cell largely decreases cell migration, our hypothesis is that targeting AuNPs to the cell nucleus region could enhance nuclear stiffness, and therefore inhibit cell migration and invasion. Therefore, we developed a strategy to inhibit cancer cell migration by targeting nucleus, by nuclear localization signal (NLS) functioned gold nanoparticles. The AuNPs that are trapped at the nuclear membrane could possibly (1) add to the mechanical stiffness of the nucleus and (2) stimulate the overexpression of lamin A/C proteins that located around the nuclear membrane, thus increasing nuclear stiffness and slowing cancer cell migration and invasion. **1.2. Targeting cancer cell integrins using gold nanorods in photothermal therapy.** Cytoskeletons are cell structural proteins that closely relate to migration, and surface receptor integrins play critical roles in controlling the organization of cytoskeletons. Therefore, we developed a strategy to inhibit cancer cell migration by targeting integrins, using RGD peptide-functionalized gold nanorods. To enhance the effect, AuNRs were further activated with 808-nm near-infrared light to generate heat for photothermal therapy, where the temperature was adjusted not to affect the cell viability/proliferation. The ability of targeting AuNRs to cancer cell integrins and the introduction of PPTT stimulated broad regulation on the cytoskeleton, which provides the evidence for a potential medical application for controlling cancer metastasis.

COLL 530

Biofragment responsive diffraction grid sensor: Using specific binding molecule conjugated hydrogel

Woo S. Jinn¹, jinnws@naver.com, Byunghoon Kang¹, Moo-Kwang Shin¹, Seungjae Oh², Byeonggeol Mun¹, Seungjoo Haam¹. (1) Department of Chemical and Biomolecular Engineering, Yonsei university, Seoul, Korea (the Republic of) (2) Department of radiology, College of medicine, Yonsei university, Seoul, Korea (the Republic of)

Advances in early diagnosis technology for severe diseases, such as cancer or neurodegenerative disease, have made it feasible to increase chance to recover diseases completely. The general method of early detection is to find out a slight change of disease-specific biomarker level exquisitely in body fluid. There exist many kinds of disease related biomarkers such as disordered DNA or microRNA, inflammatory enzymes and proteins. In particular, monitoring of proteins concentration is crucial, because disease occurrence, mainly caused by the problematic proteins, rather than that of DNA or RNA. There are several methods of measuring proteins concentration using inorganic nanoparticles or nanoarrays, polymeric nanoparticles or hydrogel based sensors. Especially, molecular reactive hydrogel based sensor using affinity binding, molecular imprinted hydrogel (MIH), is advantageous because of their simple label-free detection system, as well as high bio-applicability (implantable or wearable) and biocompatibility.

Herein, we fabricated an optical sensor using targeting moiety and silica nanoparticles (SNPs) conjugated bio-responsive hydrogel to analyze protein biomarkers by measuring diffracted light. Conformational change of biotin conjugated hydrogel was observed when avidin, as a target biomarker, exist in interconnecting hydrogel networks. Meanwhile, it is well known that uniformly arrayed nanoparticles induce different diffraction of light with their distances. Therefore in this work, 50 nm SNPs as light diffraction source were incorporated with hydrogel, showed red-shifted diffraction light with hydrogel shrunk by combining of the target protein. Protein concentration was calculated by measuring red-shift of diffracted light. Altogether, we developed well-defined label-free bio-responsive hydrogel for measuring target biomarkers, which would be widely applicable in early diagnosis of severe disease as well as bio-sensing technology.

COLL 531

Investigation of nanoscale interfacial interaction of amyloid beta peptide

Kazushige Yokoyama, yokoyama@geneseo.edu. Chemistry, The State University of New York Geneseo College, Rochester, New York, United States

The amyloid beta peptide 1-40 ($A\beta_{1-40}$) was prepared over nanogold colloidal surfaces together with Thioflavin T (ThT)dye as a fluorophore as $A\beta_{1-40}$ proceeds a folding conformational change. A series of studies on fluorescence decay time were analyzed at pH's (pH 1 – 12), and with gold colloidal sizes ranging from 10 nm to 100 nm. It was speculated that ThT attached to either ^{22}Glu or ^{23}Asp of the $A\beta_{1-40}$ through an electrostatic interaction between adjacent $A\beta_{1-40}$ monomers. The spacing between adjacent $A\beta_{1-40}$ monomers must be increased for gold colloidal sizes of 50 nm and above. We attempted to extract the ThT attachment site in $A\beta_{1-40}$, and it was speculated that the hydrophilic segment of $A\beta_{1-40}$ was used in binding to the gold colloidal surface and hydrophilic site of $A\beta_{1-40}$, networking with the other $A\beta_{1-40}$ adsorbed on the gold colloidal surface. This study provided a significant evidence supporting that $A\beta_{1-40}$ has higher binding affinity than a gold colloidal surface.

COLL 532

Temperature-controlled adhesion of bacteria and lectins to carbohydrate presenting microgel films

Tanja J. Paul¹, tanja.paul@hhu.de, Carina Spormann², Pauline Watermann¹, Sophie Rübeler¹, Thisbe K. Lindhorst², Stephan Schmidt¹. (1) Institute for Organic and Macromolecular Chemistry, Heinrich-Heine University, Düsseldorf, Germany (2) Otto Diels Institute of Organic Chemistry, Christiana Albertina University of Kiel, Kiel, Germany

Multivalent carbohydrate interactions at the cell interface play a crucial role in many biological processes, such as cell development, communication or pathogen invasion. Recent work showed that the overall binding strength can be controlled by adjusting the material parameters of carbohydrate ligand presenting polymer scaffolds, e.g. increased ligand spacing and high elastic modulus result in stronger binding. Here we harness these principles in order to design thermosensitive microgel coatings that can bind clinically relevant carbohydrate binding pathogens, such as *E. coli*, in a stimuli responsive fashion. At elevated temperature, these gels collapse and increase their elastic modulus, as well as ligand spacing, resulting in increased interactions. This process is reversible and potentially allows capturing and releasing carbohydrate binding bacteria by microgel coatings and temperature stimulus.

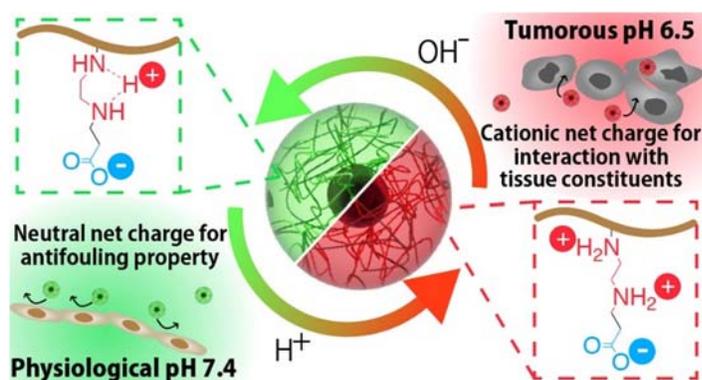
We present the synthesis of thermoresponsive carbohydrate presenting poly(*N*-isopropylacrylamide) microgels via different synthetic approaches, e.g. copolymerization of ligand monomers or post-functionalization. The influence of charged groups, ligand density and different microgel architecture on temperature dependent receptor binding and *E. coli* catch and release are investigated in dispersion by Bradford assay and on microgel films using fluorescence microscopy, as well as readout in microwell plates. We noticed that robust microgel films could be readily prepared by physisorption on plastic surfaces, which may stimulate larger scale applications of these materials. Moreover, we perform detailed analysis on the microgel structure and ligand positioning upon temperature transition. We believe that specific protein binding and bacterial adhesion are further enhanced by a smoother microgel surface and enrichment of carbohydrate ligands at the microgel surface above the phase transition temperature. Detailed studies by STED microscopy and AFM colloidal probe are underway to shed light on these phenomena.

COLL 533

Ethylenediamine-based betaine structure switches the neutral net charge of polyzwitterion into cationic at tumorous pH toward effective tumor accumulation of the coated nanomaterials

Hiroyasu Takemoto, takemoto@res.titech.ac.jp, Abdul-Hackam Ranneh, Takahiro Nomoto, Makoto Matsui, Keishiro Tomoda, Nobuhiro Nishiyama. Tokyo Institute of Technology, Yokohama, Japan

Polyzwitterions have been employed as coating polymers for biomaterials, in order to install antifouling property on the surface. In this regard, we successfully demonstrated that fine-tuning of ionizable moiety in the betaine structure builds a molecular program to switch the antifouling property to be interactive with anionic tissue constituents at tumorous condition. Carboxybetaine comprising ethylenediamine moiety enabled stepwise protonation and the di-protonation event of ethylenediamine in the betaine structure proceeded at around tumorous pH 6.5; as a result, the net charge of the developed polyzwitterion (PGlu(DET-Car)) was neutral at pH 7.4 for antifouling property, but was cationic at pH 6.5 for interaction with anionic glyocalyx (or extracellular matrices) and facilitated cellular internalization. Ultimately, the quantum dots (QDs) coated with PGlu(DET-Car) exhibited comparable (or longer) blood circulation profile, as well as more effective tumor accumulation, relative to PEG-coated QDs. The present study provides a design rationale of smart polyzwitterion with switchable property, in response to tumor-specific pH gradient, based on a precise control of the net charge.



COLL 534

Peptide nucleic acid-lipid nanodiscs for delivery of STING agonists in the tumor microenvironment

Darrell J. Irvine, djirvine@mit.edu. Massachusetts Inst of Tech, Cambridge, Massachusetts, United States

Ligands for the Stimulator of Interferon Genes (STING) receptor are potent inducers of anti-tumor immunity, primarily via immunostimulatory effects on tumor vasculature and intratumoral immune cells. STING can be activated pharmacologically by small molecule cyclic dinucleotides (CDNs), but these compounds are inefficiently taken up by cells, and rapidly pass into the systemic circulation even following local injection, raising concerns of systemic toxicity. To control the biodistribution and pharmacokinetics of CDNs, we developed a strategy to reversibly complex these compounds with nanocarriers, using peptide nucleic acids (PNAs) that can undergo base stacking with CDNs to noncovalently associate CDNs with lipid vesicles or nanodiscs. CDNs complexed with PEGylated PNA-lipid nanodiscs were effectively internalized by reporter macrophages in vitro and activated STING. We found that intratumoral administration of

CDN-loaded lipid nanodiscs could increase the antitumor activity of STING agonists over free CDN injection, especially when combined with treatment using the approved checkpoint inhibitor anti-PD1. CDN delivery promoted uptake of nanodiscs in tumor-infiltrating leukocytes. These studies suggest that exploiting noncovalent interactions of CDNs with nucleic acid structures can be used to enhance the functional delivery of these compounds in vivo.

COLL 535

Nanomedicine approaches to improve cancer immunotherapy

Andrew Z. Wang, zawang@med.unc.edu. Radiation Oncology, University of North Carolina Chapel Hill, Chapel Hill, North Carolina, United States

Cancer immunotherapy, the leveraging of a patient's own immune system to treat cancer, has emerged as an exciting new treatment strategy for advanced and metastatic disease. Recent development of antibodies that block negative regulatory molecules expressed by T cells, such as cytotoxic T-lymphocyte-associated antigen 4 (CTLA-4) and programmed cell death 1 (PD-1), have resulted in sustained clinical responses previously unseen with chemotherapy and molecularly targeted therapy. Despite this success, only 10-15% of patients experience long term durable remissions. These results have led to high interest in developing strategies to further improve cancer immunotherapy.

Several nanoparticle properties, such as immunogenicity, are uniquely suited for improving immune response. In this talk, I plan to discuss two approaches that my group has taken to utilize nanotechnology to improve cancer immunotherapy. We will discuss the use of antigen-capturing nanoparticles to capture tumor-derived antigens and improve the abscopal effect in cancer immunotherapy. We will also discuss our work on dual-immunotherapy nanoparticles that can improve immune checkpoint combination treatments.

COLL 536

Immunomodulation *in vivo* through direct cytosolic delivery of siRNA to macrophages

Joseph Hardie¹, jhardie7@gmail.com, **Ying Jiang**^{1,2}, **Yuanchang Liu**¹, **Moumita Ray**³, **Xiang Luo**⁴, **Riddha Das**¹, **Ryan Landis**¹, **Michelle E. Farkas**³, **Vincent M. Rotello**⁵. (1) University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Department of Chemistry, University of Florida, Gainesville, Florida, United States (3) Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States (4) ShenYang Pharmaceutical University, Shenyang, China (5) Univ of Massachusetts, Amherst, Massachusetts, United States

An uncontrolled inflammatory response is a key element of many diseases including rheumatoid arthritis and celiac disease. In this work, we delivered siRNA targeting TNF- α , a key signaling factor in the inflammation cascade, into immune stimulated mice using nanoparticle-stabilized capsules (NPSCs) as an immunomodulatory agent. NPSCs, which are lipid emulsions stabilized by functionalized gold nanoparticles, are capable of delivering a variety of cargoes, including siRNA, directly to the cell cytosol for effective RNAi. When injected intravenously, NPSCs rapidly accumulate in the spleen, a repository of immune cells, and deliver loaded siRNA. This capability of the NPSCs was utilized to create systemic knockdown of the TNF- α in an over-inflammation disease mouse model. LPS-challenged mice treated with NPSC/siRNA-TNF- α showed global decrease of pro-inflammatory cytokine expression in a non-toxic, specific manner. Due to its organ-targeting functionality and high biologic delivery efficacy, this system shows promise for the treatment of autoimmune and chronic inflammation disorders.

COLL 537

Immunostimulatory dual-functional nanocarriers that improve cancer immunochemotherapy

Song Li, sol4@pitt.edu. Pharmaceutical Sciences, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

Recent efforts in my lab have been focused on development of dual-functional nanocarriers that have therapeutic activity in addition to a function of delivery. Several nanocarriers have been developed that showed synergistic antitumor activity with codelivered chemotherapeutic agents in murine models of breast and prostate cancers. One such nanocarrier, PEG_{2k}-Fmoc-NLG919, is based on a PEG conjugate with NLG919, a small molecule inhibitor of indoleamine 2,3-dioxygenase 1 (IDO1) that is overexpressed in various types of cancers and negatively regulates the tumor immune microenvironment. We showed that PEG_{2k}-Fmoc-NLG alone was effective in enhancing T-cell immune responses and exhibited significant antitumor activity *in vivo*. More importantly, systemic delivery of paclitaxel (PTX) using the PEG_{2k}-Fmoc-NLG nanocarrier led to a significantly improved antitumor response in both breast cancer and melanoma mouse models.

COLL 538

Polymers and polymer assemblies with inherent pharmacologic activity to target chemokine networks in the treatment of metastatic cancer

David Oupicky, david.oupicky@unmc.edu. University of Nebraska Medical Center, Omaha, Nebraska, United States

Polymers with inherent pharmacologic activity has captured recent attention as suitable components of drug delivery systems for combination cancer therapies. Chemokine networks control cell movement to specific locations throughout the body as part of

normal homeostasis and during pathological processes such as cancer and inflammation. In tumors, a complex chemokine network controls cell trafficking into and out of the tumor microenvironment. Importantly, chemokine networks are directly involved in the molecular control of metastasis and govern organ-specific homing of metastatic cells, which makes them promising targets for the development of antimetastatic therapies. We have developed a class of polymers (PCX) with inherent ability to inhibit the CXCR4 chemokine receptor and to deliver therapeutic nucleic acids as part of combination antimetastatic therapies. I will present our progress towards development of fluorinated PCX/siRNA nanoparticles as antimetastatic therapies based on combined inhibition of CXCR4 and silencing of the signal transducer and activator of transcription 3 (STAT3) in metastatic breast cancer.

COLL 539

Protein engineering to modulate the immunostasis mediated by the PD-1 immune checkpoint

Mingnan Chen, mingnan.chen@utah.edu, Peng Zhao, Shuyun Dong, Peng Wang. Pharmaceutics and Pharmaceutical Chemistry, University of Utah, Salt Lake City, Utah, United States

Immunostasis is critical for the immune system to defend against infections and malignancy without causing autoimmune disorders. The programmed death-1 (PD-1) immune checkpoint is one mechanism that maintains immunostasis.

In autoimmune diseases, the PD-1 immune checkpoint is overridden by immune stimulatory signals, and immunostasis is hence interrupted. Under this circumstance, PD-1 expression cells or PD-1-positive cells may be viewed a pathogenic cell population. Thus, depletion of PD-1-positive cells may be beneficial to suppress autoimmunity. To enable the depletion, we engineered an immunotoxin that has selective toxicity to PD-1-positive cells. The depletion of PD-1-positive cells ameliorated autoimmune diseases in two animal models, type-1 diabetes and experimental autoimmune encephalomyelitis (EAE). Interestingly, the depletion, although drastically inhibiting autoimmunity, did not compromise healthy adaptive immunity because the depletion did not affect naive lymphocytes which are PD-1-negative. Taken together, the depletion of PD-1-positive cells may become a therapeutic approach that selectively and specifically suppresses autoimmunity and restores the immunostasis.

In cancer, some tumor cells hijack the PD-1 immune checkpoint to suppress anti-tumor immunity. Inhibitors of the PD-1 immune checkpoints have been developed to block the checkpoint and revive anti-tumor immunity. However, these inhibitors indiscriminately revive both tumor-reactive T cells and auto-reactive T cells and hence cause autoimmune toxicity. To fill this gap, we developed a protein-based nanoparticle carrier to specifically deliver the inhibitors to tumor-reactive T cells but not auto-reactive T cells. We also created a protein-based nanoparticle vaccine to amplify tumor-reactive T cells. The carrier and the vaccine potentially reduce the autoimmune toxicity of PD-1 immune checkpoint inhibitors while improve their efficacy.

In summary, protein engineering is a useful tool to modulate immunostases.

COLL 540

Bio-responsive materials for improving iron chelation therapy

May Xiong, *mpxiong@uga.edu*. *Pharmaceutical & Biomedical Sciences, University of Georgia, Athens, Georgia, United States*

For treating hereditary or acquired iron overload (IO), Deferoxamine (DFO) is one of three FDA-approved drugs. In addition to dose-related toxicity issues and short circulation times, DFO is currently unable to efficiently target the large pool of iron in the liver where a vast majority of excess iron is stored in the macrophages. In spite of these observations, surprisingly little work has focused on investigating the relationship between targeting of the liver, iron chelation efficacy *in vivo*, and the need to develop bio-responsive macromolecular systems for excreting iron-chelates from the body. In particular, environment-responsive materials capable of chelating excess iron and degrading in response to specific triggers unique to IO would be especially attractive but have yet to be thoroughly investigated. Since iron-mediated generation of highly toxic Reactive Oxygen Species (ROS) plays a major role in the process leading to iron overload-related diseases, my laboratory has been looking into design of ROS-responsive biomaterials to effectively chelate iron from macrophages while ensuring their renal and fecal elimination from the body. Bio-responsive materials for iron chelation do not induce cytotoxicity in cells nor display signs of toxicity in mice administered doses above the LD50 of free DFO. Importantly, these bio-responsive macromolecular chelators exhibit excellent iron binding and exclusion capabilities, as evidenced by decreased serum ferritin levels and improved total renal and fecal elimination of iron-bound chelates. Overall, ROS bio-responsive iron chelating materials have shown potential for efficiently and safely improving iron elimination *in vivo*.

COLL 541

Surface modified nanoparticles for photoimmunotherapy and X-ray induced photodynamic therapy

Jin Xie¹, *jinxie@uga.edu*, **Zipeng Zhen**¹, **Shiyi Zhou**¹, **Hongmin Chen**², **Weizhong Zhang**¹. (1) *Chemistry, University of Georgia, Athens, Georgia, United States* (2) *Xiamen University, Xiamen, China*

Photodynamic therapy (PDT) is an emerging cancer treatment modality. Despite the focal treatment nature, it is desired that photosensitizers are delivered to tumors with high efficiency and selectivity in a PDT process. Our recent work on using ferritin, a protein cage (~12 nm), as a photosensitizer carrier. Ferritin can encapsulate photosensitizers such as zinc hexadecafluorophthalocyanine (ZnF₁₆Pc) at high efficiency (40 wt%) and they can be modified by both chemical and genetic methods. We have successfully introduced folic acid, RGD4C, and a FAP targeting scFv, onto the surface of ferritins. We then exploited the resulting ferritin cages to navigate PDT to different components in tumors, including cancer cells, cancer endothelial cells, and

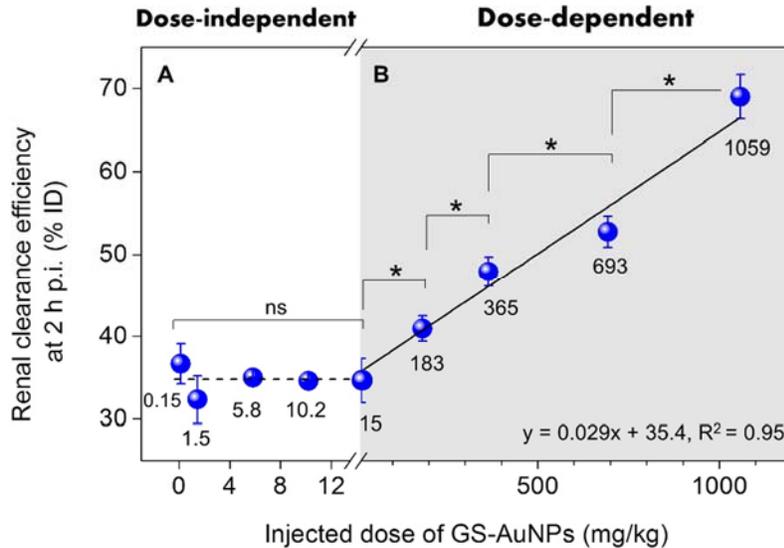
cancer associated fibroblasts (CAFs). We found that endothelium targeting PDT can enhance the tumor EPR effect to allow for more efficient nanoparticle delivery to tumors. Meanwhile, eliminating CAFs in tumors can improve CD8+ T cell penetration and thereby augmenting anti-tumor immune response. In the second half of the lecture, I will be talking about X-ray induced PDT, or X-PDT, a new technology that is developed to address the shallow penetration issue of conventional PDT. The key component of the X-PDT technology is an integrated nanosystem called X-ray nanosensitizer, which consists of: 1) a nanoparticle scintillator that converts X-ray photons to visible photons and; 2) photosensitizer whose excitation matches the emission of the scintillator. Upon X-ray irradiation, the nanoscintillator works as a transducer, producing X-ray excited optical luminescence; the visible photons, in turn, activate the photosensitizers, producing reactive oxygen species, most importantly singlet oxygen. We have shown that X-PDT can be activated from beneath thick tissues to efficiently kill cancer cells. We also found that X-PDT is more than a simple derivative of PDT; rather, it is a unique combination of PDT and radiation therapy. The two modalities target different cellular components, and the damage overwhelms cellular repairs, leading to synergistic therapy outcomes.

COLL 542

Dose dependencies and biocompatibility of renal clearable gold nanoparticles: From mice to non-human primates

Jing Xu¹, xujing_c@hotmail.com, Mengxiao Yu², Chuanqi Peng¹, Jie Zheng³. (1) Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas, United States (2) University of Texas at Dallas, Richardson, Texas, United States (3) Chemistry, UT Dallas, Richardson, Texas, United States

Dose-dependent phenomena in pharmacokinetics and clearance are well recognized in clinically used small molecules, however, very few studies have been conducted to investigate the dose-dependent behaviors of nanomedicines. Here we report our most recent study on dose-dependencies of renal clearable gold nanoparticles (GS-AuNPs). We found that pharmacokinetics and renal clearance are strongly dose-dependent when the injection doses are above 15 mg/kg: high dose accelerated the renal elimination and shortened the blood retention. As a result, the no-observed-adverse-effect level (NOAEL) of GS-AuNPs was above 1000 mg/kg in CD-1 mice. The rapid renal clearance and high biocompatibility can be translated to the non-human primates: no adverse effects were observed within 90 days after intravenous injection of 250 mg/kg GS-AuNPs. These findings and fundamental understandings of dose effects on *in vivo* transport of ultrasmall AuNPs suggest a strategy to optimize their biomedical functions and minimize their health hazard in the future clinical translation.



Dose effect on renal clearance of 2.5 nm glutathione-coated gold nanoparticles (GS-AuNPs) after intravenous injection in CD-1 mice

COLL 543

Design of lipid-protein conjugate with a self-assembling ability on a cell membrane by using microbial transglutaminase reaction

Mari Takahara¹, takahara@kct.ac.jp, **Rie Wakabayashi**², **Kosuke Minamihata**², **Masahiro Goto**², **Noriho Kamiya**². (1) Department of Materials Science & Chemical Engineering, National Institute of Technology, Kitakyushu College, Kitakyushu, Fukuoka, Japan (2) Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Fukuoka, Japan

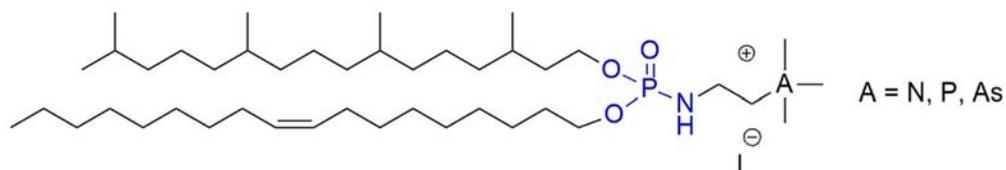
Lipid-modification of proteins plays a significant role in regulating a cellular environment. Mimicking natural lipidated protein is a key technique to assess the function of proteins modified with lipids and also to render self-assembly of lipids to a protein of interest for drug delivery system (DDS). Herein we report a novel methodology of conjugating proteins with lipid-fused peptides under physiological conditions by using microbial transglutaminase (MTG) reaction. MTG catalyzes the cross-linking reaction between specific Q in a protein and K in newly designed lipid-fused peptides. The water-soluble peptide substrates for lipid modification are represented as C₁₄-X-MRHKGS, where C₁₄, X, and MRHKGS are myristic acid, linker peptides composed of G, P, or S, and MTG-reactive K surrounded with basic amino acids, respectively. MTG-mediated cross-linking reaction between a protein fused with LLQG at C-terminal and C₁₄-X-MRHKGS (5 molar eq.) in a saline without surfactants resulted in lipid-protein conjugates with yields of 70 to 100%. Then, the obtained lipid-protein conjugates were evaluated regarding their cell membrane anchoring ability without purification. The anchoring ability of the lipid-protein conjugates onto a cell membrane depended on the number of G in the linkers of G_nS used at X moiety, where self-assembly of G_nS motif serves as an anchoring enhancer toward the membrane.

COLL 544

Synthetic phospholipids: A versatile molecular platform to design cationic amphiphiles used for nucleic acid delivery

Paul-Alain Jaffres¹, pjaffres@univ-brest.fr, **Mathieu Berchel**¹, **Amal Bouraoui**¹, **Olivier Lozach**¹, **Tony L. Gall**², **tristan montier**². (1) Chemistry, Université de Brest, CEMCA UMR CNRS 6521, Brest, France (2) INSERM U613, Gene Therapy team, BREST Cedex 02, France

The use of nucleic acid as therapeutically agent offers many perspectives of applications for acquired (cancer, tendon healing) or inherited disease (monogenic diseases). The current challenge lies in the development of carriers that can be produced on large scale, that keep their efficacies in vivo and that feature a low cytotoxicity. We have developed a molecular platform, based on phosphorus chemistry, which is adapted to prepare cationic phospholipid (figure 1) and bolaamphiphiles. Interestingly, the lipid part and the cationic polar head group (ammonium, imidazolium, arsonium...) can be easily tuned leading to noticeable differences in terms of transfection efficacies and cytotoxicity. Moreover, some cationic lipids exhibit remarkable bactericidal action thus permitting transfection of mammalian cells in presence of bacteria. Moreover, the introduction of additional functionalities (e.g. fluorescent probe) is possible while keeping a direct and efficient synthesis approach. More recently we have developed a method to control the supramolecular assembly of these cationic amphiphiles that can adopt a layered supramolecular packing or, after a functionalization by using thiol-ene click reaction, an inverted hexagonal supramolecular packing. This lecture will show the versatile synthesis of this class of cationic amphiphiles, will illustrate their physico-chemical behaviors and their in vitro and in vivo use for nucleic acid delivery.



COLL 545

Chain length and headgroup dependence of phase separation in mixed vesicles of DiA and phosphatidyl choline

Sanaz Bandegi², **Marc A. Ilies**¹, **Stephanie L. Wunder**², slwunder@temple.edu. (1) Temple University, Philadelphia, Pennsylvania, United States (2) Chemistry, Temple University, Philadelphia, Pennsylvania, United States

The alkyl chains of fluorescent lipids insert into membranes and are used to understand their biophysical properties. In this study we used a modified dialkylaminostyryl

fluorescent lipid, 4-(4-(dihexadecylamino)styryl)-N-methylpyridinium iodide (DiA), replacing the I⁻ counterion with the Cl⁻ anion to increase hydration of the polar head and to enable self-assembling in water and formation of vesicles. Vesicles composed of DMPC/DiA, DPPC/DiA, DSPC/DiA, DMPE/DiA, DPPE/DiA and DSPE/DiA have been prepared in mole ratios between 100/0 to 0/100, in order to investigate the effects of chain length and headgroup type on chain packing and phase separation in these mixed amphiphile systems, using nanocalorimetry and fluorescence data, as well as Langmuir-Blodgett trough measurements on monolayers.

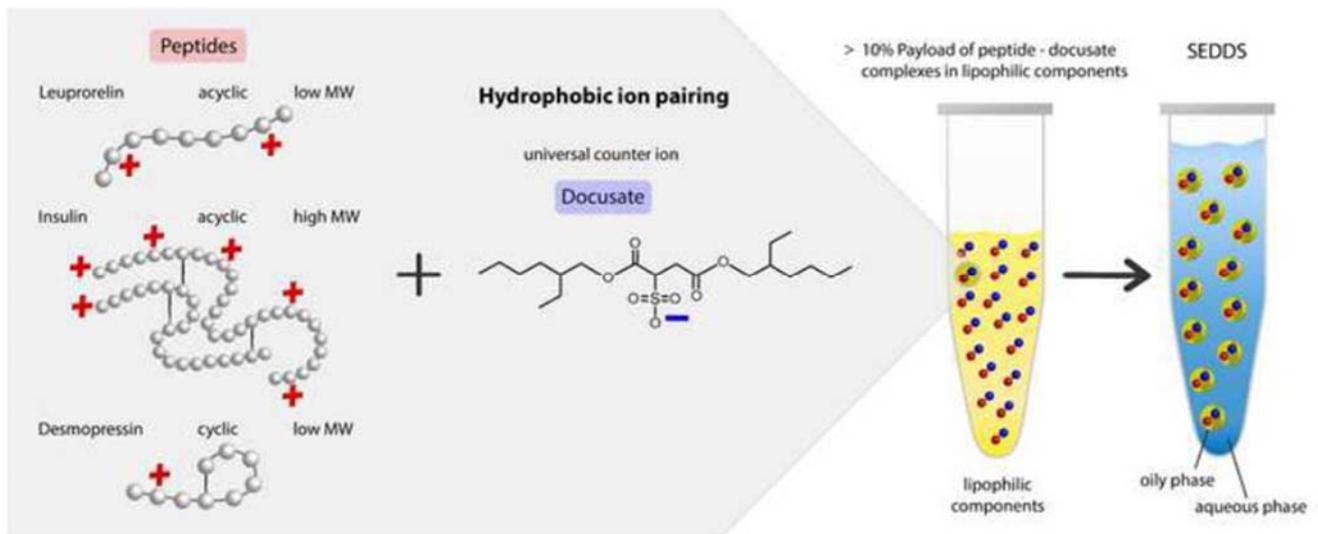
COLL 546

Advances in peptide delivery: Hydrophobic ion pairing in SEDDS for solubilization, protection, and enhanced delivery of oral peptides

Vincent Jannin^{1,2}, vjannin@Gattefosse.com, *Andreas Bernkop-Schnürch*³. (1) R&D, Gattefosse S.A.S, Lyon, France (2) Chimie et Physique, CPE Université de Lyon, Lyon, France (3) Center for Chemistry and Biomedicine, University of Innsbruck, Innsbruck, Austria

Self-emulsifying drug delivery systems (SEDDS) representing isotropic mixtures of oils, surfactants and hydrophilic cosolvents are commonly used to increase the oral bioavailability of poorly water-soluble drugs. This technology is also a promising tool to open the door for the oral administration of therapeutic peptides and proteins. Up to date, however, this promising strategy has by far not reached its full potential, as various hurdles still need to be overcome: the loading of hydrophilic peptides in lipid-based formulations, the protection of peptides against metabolic enzymes (proteases, lipases) and the reduction by glutathione, the efficient permeation of SEDDS through the mucus layer of the intestinal epithelium and finally the absorption of the large hydrophilic molecule. This presentation will present the latest results of peptide oral delivery with SEDDS where the aforementioned hurdles were overcome:

- Hydrophobic ion pairing of peptides with anionic surfactants allows reaching more than 10% payload in SEDDS with protic solvent and surfactants like Labrasol® ALF.
- SEDDS are also able to protect peptides against various metabolic enzymes (trypsin, α -chymotrypsin, elastase) and the reduction by glutathione as long as the peptide stay within the colloidal phase. The (micro)emulsions formed after dilution of SEDDS with peptides are stable in term of particle size and zeta potential for at least 4 hours and protect efficiently peptides against degradation.
- Finally, SEDDS containing Labrasol® ALF are able to increase the absorption of peptides by membrane fluidization and opening of tight junctions of the intestinal barrier.



COLL 547

Highly stable, ultrasmall liposomes with stimuli-responsive drug-release capability for cancer therapy

Bong Jin Hong¹, *b-hong@northwestern.edu*, **Aysenur Iscen**², **George C. Schatz**¹, **Sonbinh T. Nguyen**¹. (1) Chemistry, Northwestern University, Evanston, Illinois, United States (2) Chemical and Biological Engineering, Northwestern University, Evanston, Illinois, United States

While drug-loaded liposomes have garnered several notable successes as cancer treatments (e.g., DoxilTM, ONIVYDE[®], Marqibo[®], and Myocet[®]), the relatively large sizes (hydrodynamic diameter (D_H) = ~100 nm) of these early systems are still of concern as they can result in non-optimal biodistributions and severe side effects. Thus, size-reduction of these particles to 15-50 nm has been proposed as a strategy for overcoming these problems and enhancing their therapeutic efficacies in a broad range of diseases. Unfortunately, while liposomes of this size regime, commonly known as ultrasmall unilamellar vesicles (uSUVs), can be synthesized, they have very poor colloidal and membrane stabilities due to their highly strained, acute membrane curvature, which leads to payload leakage, inter-particle fusion, and lipid membrane aggregation. This presentation will show how these problems can be overcome through the integration of a stimuli-responsive poly(acrylic) acid (Chol-PAA) polymer shell into uSUVs template. The resulting polymer-grafted liposomes (PGLs) are stable for months in biologically relevant media and exhibited over 10-fold enhanced cargo retention. In addition, the polymer shell of the PGL can undergo hydrogen-bonding-induced aggregation upon acidification to release a significant amount of payload from the liposomal core, a mechanism that has been verified *in silico* by coarse-grained molecular dynamics simulations. The colloidal stability of PGLs can be further increased by crosslinking the polymer shell while maintaining the stimuli-responsive release ability at acidic target sites such as tumor microenvironment and cellular endosome and lysosome. Together with the possibility for targeting, our modular design of a polymer

shell that provide uSUVs with excellent cargo retention capability and acid-triggered drug release ability can greatly facilitate this platform for the selective delivery of anti-cancer drugs to a broad range of disease sites while reducing their side effects.

COLL 548

Use of atomistic molecular dynamics simulations for *in silico* self-assembly of nanoparticles: Opportunities and limitations

Bogdan I. Iorga, *bogdan.iorga@cnr.fr*, *Edithe Selwa*. *Institut de Chimie des Substances Naturelles, CNRS UPR 2301, LabEx LERMIT, Gif-sur-Yvette, France*

Computational methods are increasingly being used for modeling the self-assembly process of nanoparticles. For efficiency and cost-effectiveness purposes, coarse-grain and multi-scale models are generally used. Nowadays, the recent advances in computation algorithms, especially in GPU-based computation, allow the use of all-atom representations of the system and expand significantly the scope of these atomistic simulations.

We will present the evaluation of several all-atom force fields (CGenFF/CHARMM, GAFF/AMBER and OPLS-AA) for their ability to model the self-assembly of different nanoparticles. The influence of different factors (size of the system, relative ratio of the components, etc.) on the simulation outcome will be shown, and a comparison with united-atom (GROMOS) or coarse-grain (MARTINI) force fields will be provided to complete the global picture. We will highlight the advantages and limitations of each approach, as well as the potential applications in modeling the drug delivery process.

Overall, our results are in agreement with a better description of the simulation systems by the all-atom force fields, but at the cost of significantly higher computational resources requirements.

COLL 549

Molecular dynamics simulations of hydrophobins near gas, oil and water interfaces

Andres Vodopivec¹, *vodopivec.a@husky.neu.edu*, *Yuwu Chen*³, *Paul S. Russo*², *Francisco R. Hung*¹. (1) *Chemical Engineering, Northeastern University, Boston, Massachusetts, United States* (2) *Chemistry, University of Minnesota, Baton Rouge, Louisiana, United States* (3) *Center for Computation and Technology, Louisiana State University, Baton Rouge, Louisiana, United States*

Hydrophobins are nature's most surface-active proteins abundantly produced by filamentous fungi in soil and decaying vegetation. Experimental observations suggest that these protein surfactants can efficiently encapsulate oil in cylindrical 'blobs', or gases in cylindrical bubbles. Hydrophobin layers on oil droplets and air bubbles were

characterized in terms of strength and elasticity in a recent experimental study. These properties, as well as the abundance and ease of biosynthetic manufacturing of hydrophobins, suggest that they could be used in applications ranging from oil dispersion to processing of semiconducting polymers.

Here we report molecular dynamics (MD) simulation results for two hydrophobins, EAS (class I) and HFBII (class II), near interfaces involving gas, oil and water. We used the Martini coarse-grained force field, aiming at developing a fundamental understanding of the interfacial properties of these systems at the molecular level. We will present and discuss results of the potentials of mean force of the hydrophobins near the interfaces, as well as density profiles and surface tensions in our systems; the stability of nm-sized structures formed when the hydrophobins encapsulate oil in water is also assessed.

COLL 550

High-throughput wettability screening of formulations and surfaces

Tzu-Chi Kuo, tckuo@dow.com, Adam A. Lucio, Heather Wiles, Brian Orvosh, David Hayes. Core R&D Formulation Science, The Dow Chemical Company, Midland, Michigan, United States

Wettability is among the most important properties for materials since it is widely used in correlation with adhesion, surface processability, painting, and printing in various industries. Wettability is typically quantified by measuring the contact angle or the area spread from a fixed volume of a formulation on a surface. However, both methods are either labor intense to perform or lacking necessary accuracy when human judgment is involved. An automated high-throughput wettability screening method was developed by combining a multi-channel liquid handler with an adjustable imaging system. This method allows automated screening for both liquid (formulation) and substrate (surface) libraries in a single experiment in a parallel fashion, daughtering eight samples at a time from a 96 well source plate onto multiple substrate surfaces. It is shown to be capable of screening a minimum 6% difference in spreading area with a 95% confidence level with automated image analyses. The adjustable imaging system enables the robustness to handle different degrees of wetting. Three examples are used to study wettability: (1) solvent blends on injection-molded polystyrene plaques (contact angle $\sim 0^\circ$); (2) aqueous paint formulations on thermoplastic olefin substrates (contact angle $\sim 90^\circ$); (3) additive screening for organic solvent formulations on porous polyolefins membrane.

COLL 551

Competitive adsorption between nanoparticles and surfactants at the oil-water interface

Joelle Frechette, jfrechette@jhu.edu. Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States

Nanoparticles (NPs) can add functionality (e.g., catalytic, optical, rheological) to an oil-water interface. Adsorption of ~ 10 nm NPs can be reversible, however the mechanisms for adsorption and its effects on surface pressure remain poorly understood. Here we demonstrate how the competitive reversible adsorption of NPs and surfactants at fluid interfaces can lead to independent control of both the adsorbed amount and surface pressure. In contrast to prior work, both species investigated (NPs and surfactants) interact reversibly with the interface and without the surface active species binding to NPs. Independent measurements of the adsorption and surface pressure isotherms allow determination of the equation of state (EOS) of the interface under conditions where the NPs and surfactants are both in dynamic equilibrium with the bulk phase. The adsorption and surface pressure measurements are performed with gold NPs of two different sizes (5 nm and 10 nm), at two pH values, and across a wide concentration range of surfactant (tetrapentyl ammonium, TPeA⁺) and NPs. We show that free surface active ions compete with NPs for the interface and give rise to larger surface pressures upon the adsorption of NPs. Through a competitive adsorption model, we decouple the contributions of NPs wetting at the interface and their surface activity on the measured surface pressure. We also demonstrate reversible control of adsorbed amount via changes in the surfactant concentration or the aqueous phase pH.

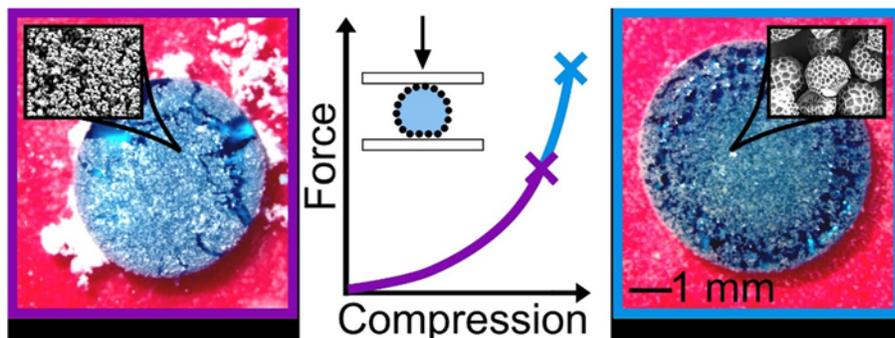
COLL 552

Elasticity and failure of liquid marbles: Influence of particle coating and marble volume

Abigail Rendos¹, arendos@bu.edu, **Nourin Alsharif**², **Brian L. Kim**², **Keith Brown**^{2,1}. (1) *Material Science Engineering, Boston University, Brookline, Massachusetts, United States* (2) *Mechanical Engineering, Boston University, Boston, Massachusetts, United States*

When coated with microscale hydrophobic particles, macroscopic liquid droplets can become non-wetting liquid marbles that exhibit many fascinating solid-like properties. Specifically, the force required to uniaxially compress liquid marbles depends on their volume, but it is unclear if the particle coating plays a role. In contrast, failure of marbles upon compression does depend on the particle coating, but the conditions for failure do not appear to change with marble volume. Here, we experimentally study the elastic deformation and failure of liquid marbles and, by applying a doubly truncated oblate spheroid model to quantify their surface area, explore the role of marble volume and particle composition. First, we find that the work required to compress liquid marbles agrees with the product of the fluid surface tension and the change in surface area, validating that the elastic mechanics of marbles is independent of the particle coating. Next, we study marble failure by measuring their ductility as quantified by the maximum fractional increase in marble surface area prior to rupture. Not only does marble ductility depend on the particle coating, it also depends on the volume with smaller marbles being more ductile. This size effect is attributed to an interaction between marble curvature and particle rafts held together by interparticle forces. Building on these results, we seek to better understand the role of interparticle interactions on marble

ductility by conducting microscopic and macroscopic experiments using particles with tunable shape and interactions. In particular, macroscopic experiments were performed on particle-laden interfaces in which the interaction forces of the particles can be tuned from weakly to strongly interactive. These experiments elucidate the analogy between ductility and the macroscopic behavior of particle-laden interfaces. Tailoring the strength of these interactions is essential for realizing controlled rupture of liquid marbles for applications ranging from smart fluid handling to pollution mitigation.



COLL 553

Isobaric vapor–liquid phase diagrams of multicomponent systems with nanoscale interfacial curvature

Nadia Shardt, Janet A. Elliott, janet.elliott@ualberta.ca. Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada

Nanobubbles, nanodroplets, and nanocapillaries are of interest to increasingly active areas of research spanning microfluidics, atmospheric physics, and drug delivery, among other fields. The theoretical understanding of pure substances at the nanoscale is well-established, but in many applications, multicomponent mixtures are present, and it therefore necessary to understand the behavior of these multicomponent systems when the vapor–liquid interface is highly curved. Phase diagrams can conveniently summarize the expected equilibrium state of a multicomponent system as a function of temperature, pressure, and overall composition. In this work, we extend our previous research that predicted isothermal phase diagrams to predict phase diagrams under isobaric conditions (constant pressure in the vapor phase). The governing equations only need the bulk properties of each component and the radius of the bubble or droplet (or the radius of the capillary) to predict the phase behavior of multicomponent systems with nanoscale interfacial curvature. In contrast to isothermal phase diagrams, isobaric phase diagrams are more difficult to calculate since additional equations are required to capture how liquid properties such as molar volume and surface tension change with temperature. For surface tension we use an approach we developed to predict multicomponent surface tensions as a function of both temperature and composition from a minimal amount of experimental data. Our proposed model accurately predicts the measured dew temperatures of a nitrogen/argon mixture in Vycor glass (pore radii of 2 nm) reported in the literature. We additionally predict the vapor–liquid phase

diagrams of methanol/ethanol and ethanol/water as a function of radius of curvature for a vapor-phase pressure of 1 atmosphere. For the nonideal ethanol/water system we compute the curvature-induced shift in the azeotrope (equal volatility point). We compare the isobaric predictions to those previously calculated under isothermal conditions.

COLL 554

Photoresponsive systems based on molecular motors

Jinling Cheng, j.cheng@rug.nl, Ben L Feringa. Dept Org Chem, Univ Groningen, Groningen, Netherlands

In Nature, light-stimulated biochemical transformation is a crucial process by which optical signals are recorded and used to trigger a variety of chemical events including photosynthesis, the process of vision, ion transport and muscle activity. Taking inspiration from integrated complex photoresponsive systems controlling dynamic functions in Nature, the design and exploration of photoswitchable molecules and materials have received major attention in the past decade. The overcrowded alkene, bis(thiaxanthylidene) and other molecular motors are particularly attractive photochromic **species** due to their fast photoisomerization, featuring an unique geometrical changes. Moreover, achieving a supramolecular arrangement of such molecules is a key challenge to fabricate assemblies where the molecules can operate in a cooperative fashion *via* light-induced geometrical changes.

Herein, photoswitchable monolayers were formed at the air-water interface from either a pure bis(thiaxanthylidene)-based photoswitchable amphiphile or from a mixture of the photoswitchable amphiphile with a conventional lipid dipalmitoylphosphatidylcholine (DPPC). Efficient photoisomerization of the *anti*-folded to *syn*-folded geometry of the amphiphile's central core induces changes in the surface pressure in either direction, depending on the initial molecular density. Additionally, the switching behaviour can be regulated in the presence of DPPC, which influences the packing of the molecules, thereby controlling the transformation upon irradiation.

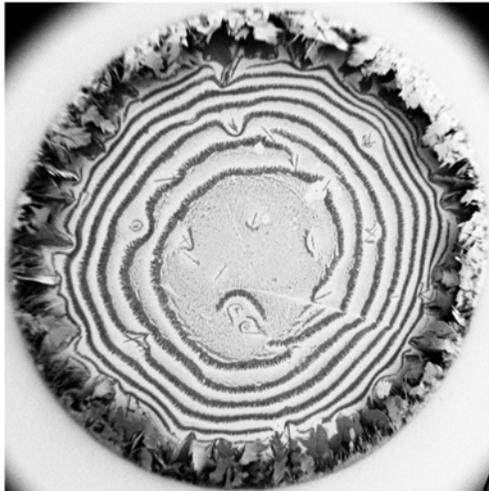
On the other hand, the properties of a liquid crystal phase is a result of the aggregation behavior of the mesogens as well as the orientation of the directors with the respect to the surfaces of the substrate and boundaries . The doping of an achiral nematic LC host with molecular motors used as chiral dopants in a cholesteric liquid crystal film will induce a rotational reorganization. The behavior and the complex flow patterns of the liquid crystals depends on the anchoring surfaces. As such, it is important to control both the modes of the aggregation and orientation, holds great promise toward future application.

COLL 555

Spirals from drops

Samantha McBride, smcbride@mit.edu, *Rachael Skye, Sami Khan, Susmita Dash, Kripa varanasi. Mechanical Engineering , Massachusetts Institute of Technology, Cambridge, Massachusetts, United States*

Spirals are one of the most common geometric motifs in both art and in the natural world, with hundreds of natural phenomena yielding spiral patterns including hurricanes, seed arrangements, seashells, and more. Here, we report on the unguided crystallization of gypsum needles into spiral formations; and specifically, into Fermat's spirals, which have the property of zero curvature at the origin and decreasing distance between subsequent arcs. These patterns are created from the evaporation of a drop on solid substrates with the unusual wetting property of having a hydrophobic advancing angle and hydrophilic receding angle. Forced crystallization via fast evaporation can induce patterns that would not regularly be observed for kinetically-limited crystal growth, and we find that spiral patterns form from a careful balance between evaporation rate and the surface pinning force. We quantify this behavior through modeling, and present a phase diagram describing when spiral patterns dominate over the more typical formation of concentric rings. In addition to being aesthetic, spirals are functional motifs with broad applications in engineered systems from antenna to microfluidics, and this technique introduces exciting possibilities for the assembly of micro-scale spiral patterns and templates.



A spiral pattern made of gypsum needles has formed from evaporation of a single drop of calcium sulfate solution on a solid substrate.

COLL 556

Molecular dynamic simulation of molecules diffusion on tracks and nanoparticles

Yanxiao Han¹, hanyanxiao1@gmail.com, *Petr Kral*². (1) *Chemistry, University of illinois at chicago, Chicago, Illinois, United States* (2) *University Illinois Chicago, Chicago, Illinois, United States*

Atomistic molecular dynamics simulations are used to explain the increased reaction rates of oligo-anionic molecular sliders with their conjugates (bromo-substituted N-methyl-Maleimide) in the presence of poly-cationic tracks. The simulations reveal that the molecular sliders not only diffuse, but also loop and hop efficiently along polymer tracks, thereby significantly increasing the meeting and reaction rates with their conjugates, in comparison to the bulk solvent. The conformational changes in the track could easily lead to oligo-anions bridging 'loops' in the track, thereby significantly increasing the effective diffusion along the track by crossing over onto a new track. Simulations of co-adsorption of a positively charged viologen-based ligand and a zwitterionic sulfobetaine ligand onto pre-saturated nanoparticles were also investigated to explain the narrow range of molar ratios of these two ligands formed on the particles. The self-limiting diffusive adsorption process is caused by electrostatic repulsion.

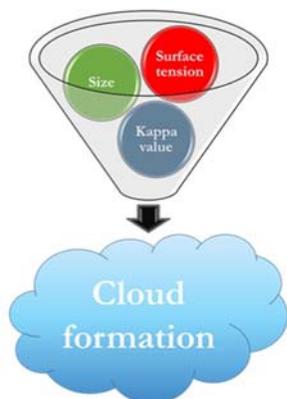
COLL 557

Surface tension measurements of model and nascent sea spray aerosol particles using atomic force microscopy

Hansol Lee¹, hansol-lee@uiowa.edu, Kamal K. Ray¹, Vicki H. Grassian^{2,3}, Alexei V. Tivanski¹. (1) Chemistry, The University of Iowa, Iowa City, Iowa, United States (2) Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States (3) Nanoengineering and Scripps Institute of Oceanography, University of California, San Diego, La Jolla, California, United States

Surface tension is an important interfacial physical property that strongly influences how efficiently an atmospheric aerosol forms clouds, which affects both regional and global climates. Specifically, sea spray aerosol (SSA) was previously shown to aid in global cooling. However, direct surface tension measurements of model and nascent SSA particles are rare, due to experimental limitations. Here, atomic force microscopy is used to directly measure the surface tension of individual, substrate-deposited SSA particles as a function of relative humidity. Model systems including electrolyte salts, surfactants, and saccharides are used to identify the experimental limitations of this methodology. For particles with a viscosity below 100 Pa s in, the AFM single particle data show excellent overlap with bulk solution surface tension measurements at overlapping concentration ranges. Following this validation, the methodology was applied to the nascent SSA particles, produced from a realistic ocean environment during two consecutively induced phytoplankton blooms. Absolute values of the surface tension of individual particles from the first bloom were up to 45% lower than the surface tension value of pure water, which is the current assumption used in climate models. These observations provide direct evidence of the role of organics in significantly depressing the surface tension of SSA particles, which has strong implications for their cloud condensation nuclei activation. Interestingly however, SSA from the second bloom show a smaller depression of surface tension due to differences in enzyme activity within the seawater. Moreover, our data indicates potential large discrepancy in predictive climate models that use overly simplistic assumptions of particle composition

and surface tension values, which does not account for complex biological activity of the ocean.



COLL 558

Experimental framework for understanding intermolecular interactions in carbon dioxide-water mixtures for EOR and storage

Richa Sharma, *rsharma15@slb.com*, Quincy K. Elias, T S. Ramakrishnan. Schlumberger Doll Research, Cambridge, Massachusetts, United States

The injection of carbon dioxide (CO₂) into reservoirs for enhanced oil recovery (EOR) is a mature technology in the petroleum industry. This work is motivated by the recent interest in using CO₂-EOR to support CO₂ storage, which can retain the benefits to commercial oil producers and also support environmental targets on carbon capture and storage. To ensure the twin goals of oil extraction and underground CO₂ storage, we need to increase the effectiveness and kinetics of at least two trapping mechanisms: (i) Solubility trapping; and (ii) Structural trapping. The first mechanism is enabled by EOR operations that alternate between CO₂ and water flooding, resulting in the dissolution of CO₂ in aqueous phase. In CO₂-EOR, which is a tertiary phase technique, the sequenced CO₂ and water injection operations are designed to mitigate the viscous fingering of low viscosity fluid. However, its effectiveness for both CO₂-EOR and storage crucially depends upon the properties of CO₂-water mixture. Similarly, the second mechanism utilizes the (undamaged) seal of geological reservoirs as trapping sites for CO₂ storage, and again the interaction between CO₂ and water molecules play an important role in the effectiveness of storage. This presentation will discuss our experimental framework for better understanding of CO₂-water intermolecular interactions in the context of above-mentioned trapping mechanisms. Specifically, we utilize two complementary sets of techniques---interfacial tension measurements and Raman spectroscopy--- and present our results for a range of temperature and pressure conditions. The key contribution of our research is the study of intermolecular interactions for equilibrated CO₂-water mixtures as opposed to first contact properties. The former is relevant for reservoir flooding since local equilibrium is established fairly

quickly compared to displacement time-scales. Our inferences may then be used for reservoir simulation and a systematic evaluation and design of optimal CO₂-EOR and storage operations.

COLL 559

Exploring new avenues of particle charging in apolar media

Benjamin Ponto, *pontob@uw.edu*, John C. Berg. University of Washington, Seattle, Washington, United States

Charging nanoparticles in liquid media of ultra-low dielectric constant ($\epsilon=2$), ie., “apolar media”, with oil-soluble surfactants has been investigated for decades. The ability to control and understand particle charging in apolar media has led to advanced digital printers (e.g., HP Indigo®) and electrophoretic displays (e.g., the Amazon Kindle). Previous work from our lab has investigated the surfactant mediated acid-base charging mechanisms of oxides and similar particles where it has been shown that the sign of particle charge can be determined by comparing the acid-base properties of a particle, ie. point of zero charge (PZC), to an experimentally determined “effective pH” of a surfactant molecule. The exploration of these mechanisms continues in three new avenues.

First, previously studied particles have only had one charging mechanism in water which is acid-base. Clay particles, which have two known aqueous charging mechanisms, were studied to determine if and how they would charge in apolar media. Second, previous studies only investigate the acid-base charging of particles in single surfactant systems in apolar media; however, it would be advantageous to be able to tune the surfactant acid-base properties by mixing surfactants with different effective pH values. This would allow the practitioner to be able to accurately control the sign and magnitude of nanoparticle charge in apolar media.

Third, while particle charging has been studied in aqueous ($\epsilon=80$) and apolar ($\epsilon=2$) media, limited study has been conducted in solvents with intermediate dielectric constants commonly referred to as leaky dielectrics. Exploring particle charging in leaky dielectrics is of interest because not only will surfactants play a role in the acid-base particle charging mechanisms, but, as the polarity of the solvent increases, acid-base interactions between the solvent and the particle surface are known to occur, as well.

COLL 560

Directing colloid motion in nematic liquid crystals near wavy boundaries

Kathleen J. Stebe, *kstebe@seas.upenn.edu*. Chem Biomole Dept Rm 311A, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States

The ability to dictate the trajectories and docking sites of microscopic objects has far-reaching implications in fields ranging from reconfigurable materials to intelligent systems. Diverse approaches have been developed, ranging from the use of external

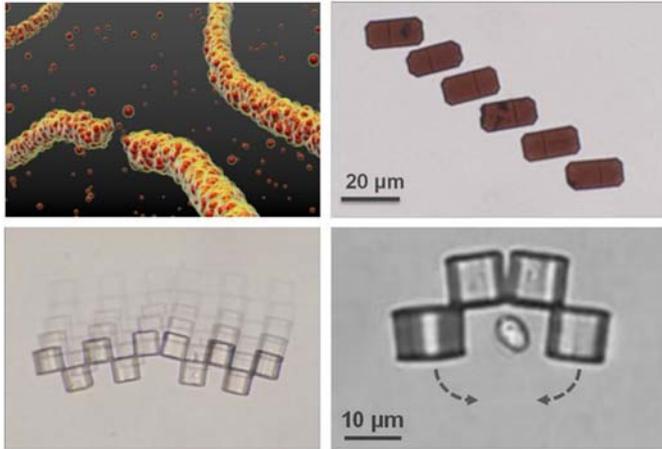
fields or of active colloids near structured boundaries. Here, we exploit confined nematic liquid crystals (NLCs) near undulating boundaries to embed energy landscapes. Related concepts have been widely explored for NLCs that create defects that trap colloids. Here, we take a different approach, and design a director field that, in the absence of the colloids, is defect-free. This field gently guides colloid motion, avoiding trapped metastable states. Since the field is related to NLC orientation, the interactions are reconfigurable, either by reorientation of the NLC under applied fields, or by reconfiguration of the boundary shape. We show that a simple boundary of alternating hills and wells embeds energetic cues that dictate particle paths and multi-stable equilibrium loci. Furthermore, we demonstrate remarkable control over the defect structure associated with the colloid, a significant outcome, since such defects attract surfactants and nanoparticles. This means of directing colloid motion is readily combined with other fields to afford additional control with promise in reconfigurable systems and in microrobotics applications.

COLL 561

Field-driven assembly, manipulation, and propulsion of dynamic structures made of particles

Orlin D. Velev, odvelev@ncsu.edu. Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States

We will discuss the principles of microscale engineering of dynamically reconfigurable and motile assemblies from multiple classes of colloidal particles. Examples of such assemblies include reconfigurable gel networks, shape-changing clusters, and self-propelling microbots. The making of such structures requires techniques for creating flexible bonds and directing particle-field and particle-particle interactions. In the first part of the talk, we will present magnetically-responsive and self-repairing gel networks and inks for 3D printing based on multiphasic liquid/liquid/solid systems. These are made of superparamagnetic nanoparticles dispersed in water, magnetically assembled into filaments, and bound by nanocapillary liquid bridges. The capillary binding allows for easy particle rolling and sliding, resulting in ultra-high filament flexibility and responsiveness. In the second part of the talk we will describe how complex magnetic polarization patterns on metallo-dielectric microcubes lead to multidirectional interactions and assembly of reconfigurable microclusters. These sequence-encoded clusters can be reversibly actuated and spatially transported by magnetic fields. They can be designed to be self-motile in media with non-Newtonian rheology. We analyze the propulsion dynamics of these active clusters based on a "coupled scallop" model and showcase their ability to grab and transport target micro-objects, hence serving as prototypes of microbots and colloidal origami. Finally, we will describe how electric fields can be used to introduce further levels of functionality in powering and controlling motile circuit-containing particles of complex shape, structure, and internally programmed response.



COLL 562

Nanostructured functional hydrogels as an emerging platform for renewable energy and environmental technologies

Guihua Yu, ghyu@austin.utexas.edu. Materials Science and Engineering, The University of Texas at Austin, Austin, Texas, United States

Nanostructured materials have become critically important in many areas of technology because of their unusual physical/chemical properties due to confined dimensions. Owing to their intrinsic hierarchical micro-/nano-structures, unique chemical/physical properties and tailorable functionality, hydrogels and their derivatives emerge as an important class of functional materials and have received increasing interests in the scientific community. Bottom-up synthetic strategies to rationally design and modify their molecular architectures enable nanostructured functional hydrogels to address several critical challenges in renewable energy and environmental technologies.

In this talk, I will present nanostructured functional hydrogels, particularly those based on conductive polymers, as an emerging powerful material platform for a number of significant applications in energy and environmental technologies, including high-energy lithium batteries and supercapacitors, solar steam generation and water desalination. I will further illustrate 'structure-derived multi-functionality' of this special class of materials.

COLL 563

Probing and understanding interfaces and interphases in electrochemical energy storage systems

Shirley Meng, shirleymeng@ucsd.edu. University Of Cal. San Diego, La Jolla, California, United States

In fundamental studies of energy storage systems, particularly electrochemical energy storage (EES), *ex situ* experiments often provide limited insights due to sample preparation and transfer. More importantly, electrochemical systems often operate at states far from equilibrium, which requires operando characterization. On the other hand, the EES systems' macroscopic properties such as the energy and power density are often governed by the electrode/electrolyte interfaces that by nature are of atomic and nano scales. In this work new findings on surface and interface stability affecting the electrochemical longevity of the high voltage cathode material are investigated using a combination of *in situ* and *ex situ* imaging and spectroscopic tools, including: transmission X-ray microscopy, synchrotron X-ray absorption spectroscopy, and double-aberration-corrected scanning transmission electron microscopy. These tools unveil that cation migration and subsequent surface structural changes at the atomic levels are majorly responsible for the degradation. Combining the DFT + *U* calculations with our experimental observations, a correlation between these interface structural instability and the capacity degradation can be established. I will extend some of the tools capabilities to studying lithium and silicon based anode materials, whose interfaces/interphases are extremely complex and dynamically changing with respect to factors such as electrolytes, current density etc. Novel techniques utilizing cryogenic microscopy are necessary to probe and understand the interfaces and interphases in these systems.

COLL 564

On demand release of bacteria from microwell arrays

Andre van der Vlies¹, ajvander@ksu.edu, Niloy Barua¹, Priscilla Guzman², Tom G. Platt², Ryan R. Hansen³. (1) Chemical Engineering, KSU, Manhattan, Kansas, United States (2) Division of biology, KSU, Manhattan, Kansas, United States

Gaining a better understanding of the biological behavior of pathogenic microorganisms is important both in the human and plant sciences. In most systems, microbes exist in communities, consisting of a complex milieu of unique species that may promote or inhibit the pathogen. Because of this inherent complexity, it is difficult to study microbe-microbe interactions in a high-throughput manner with standard microbiology tools. To address the problem, we are developing a microwell array as a high throughput screening tool to study these interactions. The platform is designed to combine a fluorescently-labeled pathogen, i.e. the focal species, with a small number of community members through a stochastic seeding process. Wells are monitored in parallel to identify those wells where focal species growth is inhibited or promoted. However, in order to identify the bacteria responsible for the interaction, it is necessary to retrieve the bacteria from individual microwells of interest for 16S rRNA sequencing. Here, we present the concept and initial experiments of a microwell array with on-demand release of bacteria from selected microwells. As a model bacterium, we use *Agrobacterium tumefaciens*, the agent of crown gall disease in plants. The key feature of the platform is the attachment of a photo-degradable membrane onto the microwell array that allows for nutrient exchange but prevents motile bacteria from escaping the wells. The

photoreactivity of the membrane allows for spatiotemporal control of degradation using a patterned illumination tool, enabling removal above targeted microwells at micron-scale resolution. For fabrication, cells are first seeded into wells using a novel seeding procedure, then the membrane precursor solution containing a photodegradable PEG diacrylate polymer and a four-arm poly(ethylene glycol) (PEG) thiol crosslinker is pipetted over the substrate. A Michael-type thiol-acrylate addition reaction generates the cross-linked polymer membrane. Irradiation of the membrane with light using the Polygon illumination tool degrades the polymer network and opens the microwells allowing bacteria to move out. By simply washing the substrate, the bacteria can be isolated for further characterization. Currently we are developing methods that allow for transfer of bacteria from several wells to agar for further characterization.

COLL 565

Degradation of protein coronas when exposed to the proteolytic environment of the pancreatic ductal adenocarcinoma cell line PANC1

Cristina Rodriguez-Quijada², cristina.rodrique002@umb.edu, Helena de Puig¹, Maria Sánchez-Purrá², Chandra Yelleswarapu², Jonathan Celli², Kimberly Hamad-Schifferli^{2,1}. (1) Massachusetts Institute of Technology, Boston, Massachusetts, United States (2) University of Massachusetts Boston, Boston, Massachusetts, United States

Gold nanoparticles have gained attention in cancer research as theranostic platforms for their easily functionalization with drugs and biomolecules for drug delivery and gene therapy purposes. Nevertheless, their exposure to biological fluids result in the spontaneous formation of a protein corona. The biocorona changes the nanomaterial's surface composition and physicochemical properties, hindering their function as therapeutic or diagnosis tools. Intense effort has been put toward understanding protein corona formation when the nanoparticle is exposed to a static environment, such as a solution of human serum. While it is well known that protein corona evolves from one biological surrounding to another due to the weak protein-NP bonds, the protein corona behavior at the tumor microenvironment is still not completely understood. The aggressive conditions at the tumor microenvironment such as high protease activity and acidic pH, can affect the protein corona in a manner completely different than other healthy tissues. In particular, matrix metalloproteinases (MMP) are present at high concentrations. Here we studied the degradation of protein coronas when exposed to the high proteolytic activity of PANC1 cell line. In addition, we explored different protein corona compositions to vary the biocorona degradation rate by using preformed coronas made of pure human serum albumin, human serum, and collagen IV, a substrate of MMP9. While there has been some work in designing coronas for their carrier properties, a study of how to optimize their properties for its degradation has been relatively unexplored. Results can allow the engineering of protein corona properties for optimal biodistribution, stability, cell interaction, and uptake.

COLL 566

Biological identity and receptors recognition of graphene nanoflakes dispersions

Valentina Castagnola, *valentina.castagnola@cbni.ucd.ie*, Luca Boselli, Maria Cristina Lo Giudice, Fatima Alnasser, kenneth dawson. University College Dublin, Dublin, Ireland

Graphene has raised high expectations for its potential applications not only in the field of electronics, composite materials, energy generation and storage, but also in biological fields, due to its distinctive properties. However, our knowledge on the factors that influence its interaction with living systems is still very incomplete.

We recognize that besides size and shape, it is the biomolecular recognition motifs conferred by the protein corona layer which lead to most early stage biological impacts, governed for example by receptor interactions, likely to determine organ-level interactions (such as, for instance, liver clearance). Therefore, the study of biological impact of nanomaterials will require surface presentations that are representative of real exposure conditions in blood.

In this work we exfoliate graphene nanoflakes directly in the presence of the biological milieu of interest, without affecting the graphene properties or compromising the protein functionality. Starting from this material we could isolate and analyze the graphene-corona complexes; while some of the proteins identified are common to many other nanomaterials, some typical ones are absent (apo B100), and some unusually abundant (for example apo A-I). For apo A-I, relevant recognition motifs at the surface of graphene were mapped by using different immunoprobes able to recognize domains proxy for the High Density Lipoprotein complex receptor binding domains.

Given the functionality and availability of such domains we investigated more in details the interactions between graphene nanoflakes and specific overexpressed cell receptors able to engage with the key motifs identified on the graphene surface. The evidences accumulated showed that these key motifs mediate early biological interactions. This certainly suggests that graphene could have distinct early biological interactions both at cell and organ level and will have to investigate this in more detail in order to promote a safe transition of graphene for biological applications.

COLL 567

Supported lipid bilayer microfluidics for gene delivery

Jason N. Belling¹, *jasonbelling@gmail.com*, Joshua A. Jackman^{2,3}, Liv K. Heidenreich⁴, Lisa M. Kawakami¹, Thomas D. Young¹, Leonardo Scarabelli¹, Chuanzhen Zhao¹, Nam-Joon Cho^{2,3}, Steven J. Jonas^{5,7}, Paul S. Weiss^{1,6}. (1) Chemistry, Biochemistry, and California NanoSystems Institute, University of California Los Angeles, Los Angeles, California, United States (2) Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore (3) Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore (4) Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles,

California, United States (5) Pediatrics, Children's Discovery and Innovation, David Geffen School of Medicine, and Eli & Edythe Broad Center of Regenerative Medicine and Stem Cell Research, University of California Los Angeles, Los Angeles, California, United States (6) Materials Science and Engineering, University of California Los Angeles, Los Angeles, California, United States (7) California Nanosystems Institute, University of California Los Angeles, Los Angeles, California, United States

Gene-editing tools are leading to a new era of personalized medicine and healthcare, and there is strong demand for the development of scalable technologies to edit the genomes of individual cells with high efficiency and speed. Towards this goal, microfluidic systems have emerged as a promising technology that facilitates intracellular delivery of biomolecular cargo based on rapid cell squeezing. As microfluidic technologies transition from conceptual prototypes to functional tools, there is a need to develop next-generation platforms with sustainable processing throughputs where a key objective is to avoid cell clogging. We report a versatile method to passivate microfluidic channels based on noncovalent lipid bicelle technology, leading to dramatic improvements in blocking efficiency against nonspecific protein adsorption and cell adhesion as compared to covalent polymer options. The functional properties of supported lipid bilayers formed *via* bicelle attachment on both glass and polydimethylsiloxane surfaces were evaluated, including membrane fluidity, passivation against nonspecific protein adsorption, and inhibition of cell attachment. This surface functionalization approach is now being explored to coat constricted microfluidic devices for the intracellular delivery of biomolecules into cells. This bicelle-based coating strategy enables inhibition of nonspecific protein and cell attachment and is poised to increase the device lifetimes and efficiency of cell transfection.

COLL 568

Layer-by-layer nanoparticles for cytokine delivery against cancer

Antonio Barberio¹, barberio@mit.edu, **Santiago Correa**³, **Erik C. Dreaden**⁴, **Talar Tokatlian**⁴, **Mariane Melo**², **Darrell J. Irvine**³, **Paula T. Hammond**¹. (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Massachusetts Inst of Tech, Cambridge, Massachusetts, United States (3) Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (4) MIT, Cambridge, Massachusetts, United States

This work focuses on delivery of cytokines, in particular a single chain interleukin-12 (IL-12), using electrostatic layer-by-layer (LbL) nanoparticles to mitigate toxicity while maintaining efficacy. Immunotherapy has become an increasingly attractive target for treatment of various cancer types with recent successes of CAR-T cell therapy and anti-PD1 treatments. An additional option for this type of immune treatment is delivery of a general immune stimulant, such as a cytokine, to the tumor microenvironment. IL-12 therapy was attempted in the past but failed due to its high systemic toxicity. This work uses electrostatic LbL technology on a nanoparticle carrier to incorporate materials

designed to abrogate systemic toxicity and increase targeting to the tumor microenvironment for IL-12 therapy. The delivery system is designed as a negatively charged liposome, with charged polymers layered alternately around it to form a multilayer thin film coating that impacts stealth, stability, release and trafficking. One of the most important challenges in such a particle system for IL-12 therapy is maintaining the protein's activity with the surface bound cell membrane receptor, while avoiding uptake and internalization that could lead to endosomal degradation and inactivity. The particle must be able to target the tumor microenvironment, but it must also effectively target T and natural killer cells that carry the IL-12 receptor. Different surface chemistries were probed *in vitro* to determine the optimal LbL particle design pertaining to the outlined criteria. The final carrier shows persistent extracellular cytokine activity *in vitro*. *In vivo* tests show that the LbL particle maintains efficacy against tumors with drastically reduced systemic toxicity.

COLL 569

Tuning non-covalent interactions for multiple cargo encapsulation inside P22 VLPs

Hitesh Kumar Waghwanī¹, hwaghwan@iu.edu, Chi-Yu Fu², John Johnson², Trevor Douglas¹, Masaki Uchida¹. (1) Chemistry, Indiana University Bloomington, Bloomington, Indiana, United States (2) Department of Integrative Structural and Computational Biology, The Scripps Research Institute, La Jolla, California, United States

The goal of this research is to use natural strategies of cargo packaging inside protein cages for the synthesis of novel bio-inspired nanomaterials. Nature utilizes non-covalent interactions between the simple protein building blocks to form complex hierarchical structure with high density cargo packaged during or after self-assembly of a range of protein cage architectures. Inspired by nature, research in our group is focused on exploring both *in vivo* and *in vitro* self-assembly approaches to package protein cargo inside P22 virus like particles (VLPs). In this research, multiple ferritin proteins (12 nm) were packaged as cargos inside P22 VLPS during self-assembly forming P22Fn (~60 nm) with a 'cage-inside-a-cage' morphology. To further modulate cargo packaging, a negatively charged variant of green fluorescent protein, (-)GFP, was packaged as a secondary cargo inside the preformed P22Fn cage by tuning non-covalent interactions between cargos. By manipulating non-covalent interactions between cargo species, we have demonstrated to control the packaging of multiple biologically relevant cargo species under mild *in vitro* conditions.

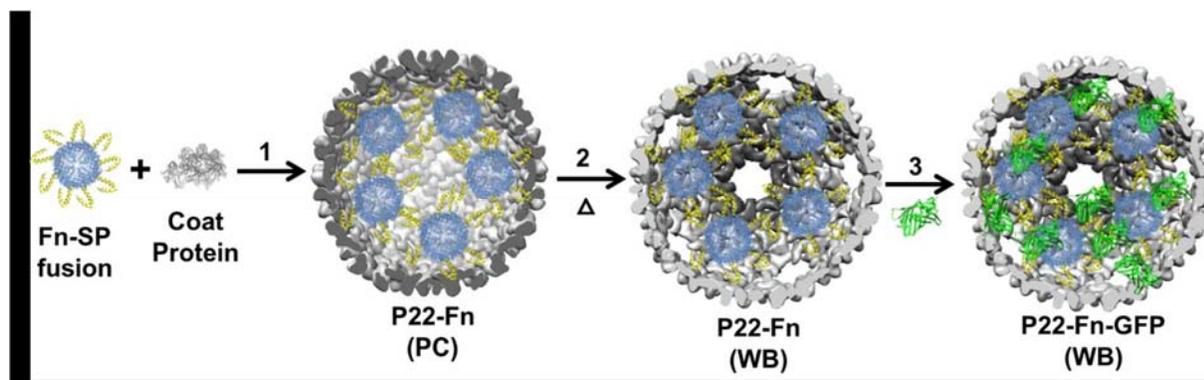


Figure. Scheme showing protein cargo encapsulation inside P22 virus-like particles during and after self-assembly. 1. Ferritin cargo encapsulation inside P22 by either in vivo or in vitro self-assembly forming P22Fn procapsid morphology; 2. Structural transformation of P22Fn from procapsid to wiffle ball morphology; 3. Accumulation of negatively charged variant of GFP inside P22Fn(WB) showing cargo encapsulation in a preformed cage.

COLL 570

OBP fused with cell-penetrating and anchor peptides promotes liposomal transduction of 1-aminoanthracene

Filipa Gonçalves¹, filipa.goncalves@ceb.uminho.pt, **Tarsila G. Castro**¹, **Eugenia Nogueira**¹, **Ricardo Pires**^{3,4}, **Rui L. Reis**^{3,4}, **Carla Silva**¹, **Artur Ribeiro**¹, **Artur Cavaco-Paulo**^{1,2}. (1) Centre of Biological Engineering, University of Minho, Braga, Portugal (2) University of Minho, Braga, Portugal (3) 3Bs Research Group – Biomaterials, Biodegradables and Biomimetics, University of Minho, Headquarters of the European Institute of Excellence on Tissue Engineering and Regenerative Medicine, Ave Park, 4806-909, Taipas, Guimarães, Portugal (4) ICVS/3Bs - PT Government Associate Laboratory, Braga, Portugal

We designed five new odorant binding proteins (OBP-I) to improve the internalization of odors into liposomes. OBP-I was fused with three cell-penetrating peptides (CPPs), namely Tat (**OBP::Tat**), pVEC (**OBP::pVEC**) and Pep-1 (**OBP::Pep-1**); and with SP-DS3 peptide (**OBP::SP-DS3** and **OBP::(GQ)₂₀::SP-DS3**).

The proteins were expressed in *Escherichia coli* BL21(DE3) and characterized regarding their molecular weight, binding ability and secondary structure content. A new methodology using liposomes as reservoirs, OBPs as carriers and 1-aminoanthracene (1-AMA) as a model molecule was developed. The internalization efficiency revealed to be dependent on the initial capacity of OBPs to bind 1-AMA, on the penetration of liposomes promoted by the CPPs and on the anchoring promoted by SP-DS peptide. An encapsulation efficiency of 42% was obtained with OBP::Tat fusion protein while the binding of 1-AMA to functionalized liposomes revealed a maximal binding of 69% for liposomes containing OBP::(GQ)₂₀::SP-DS3.

Our approaches offer new liposomes-OBP conjugates with potentialities to mediate molecules capture for the surroundings for textile and cosmetic applications.

COLL 571

Enhancement of Cas9 RNP delivery using a small molecule caged surfactant

Joachim Justad Roeise¹, joroiei@berkeley.edu, Jie Li², Aaron Taing¹, Lienna Chan², Kanav Thakker³, Niren Murthy². (1) Chemistry, University of California, Berkeley, Berkeley, California, United States (2) Bioengineering, University of California, Berkeley, Berkeley, California, United States (3) Chemical Engineering, University of California, Berkeley, Berkeley, California, United States

The lysosomal degradation of endocytosed biotherapeutics is a central problem in drug delivery. Although a wide number of proteins, polymers and peptides have been developed that can disrupt endosomes, incorporating them into delivery vehicles is challenging because of their large size (5-10kDa and above) and complicated chemistry. In this report we present for the first time a general strategy for generating small molecules that are endosomal disruptive agents, termed caged surfactants. The caged surfactants are composed of Triton X-like surfactants that have their hydrophobic segment “masked” by two hydrophilic PEG chains, which have been conjugated via acetal linkages. The caged surfactants are not membrane disruptive at pH 7.4 because of their PEG chains. However, after endocytosis, the caged surfactants become membrane disruptive because the acidic environment of the endosome hydrolyzes the PEG chains off the caged surfactants. The caged surfactants were shown to hydrolyze and release free surfactant in a pH-catalyzed manner, with a k_{2nd} of $261 \text{ s}^{-1}\text{M}^{-1}$. We demonstrate here that this property allows the caged surfactants to disrupt red blood cell membranes more efficiently at pH 6.0 than at pH 7.4. In addition, we show here that the caged surfactants can dramatically increase the ability of lipofectamine to deliver Cas9 RNPs *in vitro*. Delivery of a Cas9 RNP designed to disrupt the GFP segment of a GFP-positive HEK293 cell line was delivered with lipofectamine with and without the caged surfactant. Gene editing was then measured as the amount of GFP knockdown. This resulted in a doubling in gene editing from 12% to 24% in the presence of the caged surfactant. The caged surfactants therefore have tremendous potential for enhancing the delivery of biomolecules given their small size and well defined chemistry.

COLL 572

Sugar-grafted cyclodextrin as drug carrier for intravesical therapy for bladder cancer

Min Li, En Tang Kang, Edmund Chiong, **Koongee Neoh**, chenkg@nus.edu.sg. National University of Singapore, Singapore, Singapore

Bladder cancer is the costliest cancer to treat because about 70% of patients with superficial disease will develop tumor recurrence, thus requiring long-term follow-up and repeat interventions. One of the major shortcomings associated with current intravesical chemotherapy is the short residence time of the drug in the bladder since much of it is

lost upon the first voiding of urine. Our work focuses on the development of nanocarriers for chemotherapeutic agents to potentiate their activity against bladder cancer. Since cancer cells are known to display enhanced sugar uptake, we hypothesized that drug carriers with grafted sugar molecules will entice these cells to take in the carrier with the loaded drug, thereby promoting the delivery of the drug into the cells. Our nanocarriers were prepared from β -cyclodextrin (CD) grafted with D-glucose via azide-alkyne click reaction. Hydrophobic drugs such as doxorubicin and mitomycin C can be readily loaded in this carrier. Our experiments with UMUC3 human bladder cancer cells showed that the IC₅₀ values of chemotherapeutic drugs loaded in the sugar-modified CD nanocarriers are indeed substantially lower than those of the free drugs or drugs loaded in CD nanocarriers without grafted sugar molecules. These findings indicate that the sugar-grafted CD is potentially a promising candidate as an intravesical drug delivery system.

COLL 573

Photochemical synthesis and photocatalysis with atomically precise metal clusters

Kevin Stamplecoskie, kevin.stamplecoskie@queensu.ca. Chemistry, Queen's University, Kingston, Ontario, Canada

Nanomaterials synthesis has advanced rapidly over the past several decades, for the most part overshadowing similar strides in the synthesis of atomically precise clusters. A large bank of different clusters, with variations in stabilizing ligands, the choice of metal or alloy, and/or the number of metal atoms, have been isolated. The synthesis of clusters still presents challenges to even strong synthetic chemists. We have developed a photochemical method for the synthesizing Au₂₅SR₁₈ clusters that provides some synthetic advantages, and an opportunity to isolate new clusters.

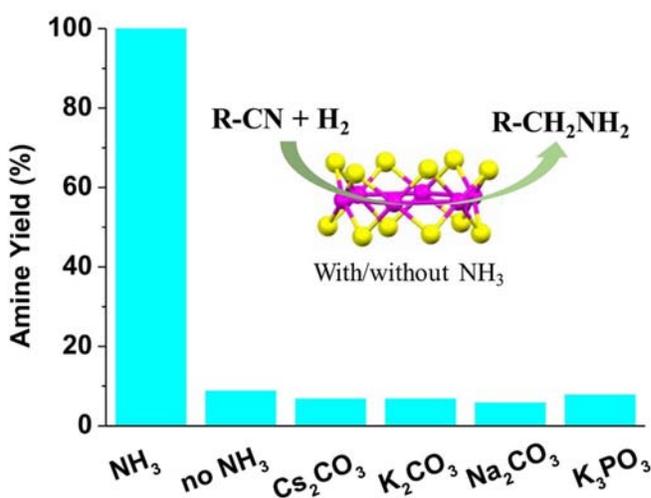
The unique optical properties of clusters will also be highlighted in this seminar, especially as they relate to the structure function-function relationship in photonic devices. The distinctive properties of individual clusters have made them attractive candidates for biomedical imaging, catalysis, photonic devices, and light harvesting. The incorporation of atomically precise clusters in photovoltaic devices will be discussed in detail, as well as the use of photovoltaics to help elucidate some of the properties of clusters that are fundamental to their use in light harvesting and other applications as well.

COLL 574

Catalytic hydrogenation of nitriles over atomically precise nickel clusters with a double-crown anatomy

Yan Zhu, zhuyan@nju.edu.cn. Chemistry, Nanjing University, Nanjing, China

Atomically precise metal clusters stabilized by organic ligands have drawn extensively interest, and these monodisperse clusters have particular potential for shedding light onto the long puzzling area of heterogeneous catalysis such as inherent size polydispersity. In many traditional catalytic reactions, however, the reactivity of metal clusters is frequently found to be passivated where the active sites on the surface metal atoms are blocked by the ligand molecules. Therefore, of particular interests are the studies involving triggering the catalytic ability of metal clusters with no need to remove any ligands via thermal treatments that usually destroys their atomically precise structures. Herein, with the determination of $\text{Ni}_6(\text{SR})_{12}$ (where SR denotes thiolate) structure, where Ni atoms are fully coordinated with thiolate molecules, the catalytic activity of $\text{Ni}_6(\text{SR})_{12}$ for nitriles hydrogenation toward primary amines could be significantly enhanced with the assistance of NH_3 molecules that positively suppress the ligand shielding effect.



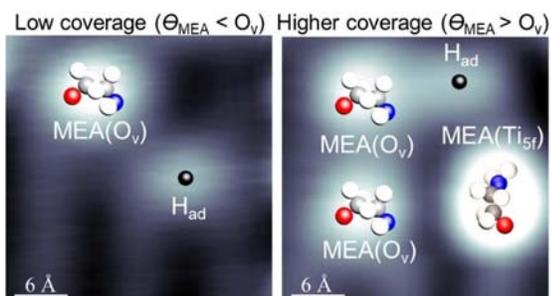
COLL 575

Defect-associated adsorption of monoethanolamine on $\text{TiO}_2(110)$ surface: From single molecules to a monolayer

So-Dam Sohn¹, sodami@unist.ac.kr, **Su-Hwan Kim**², **Sang Kyu Kwak**², **Hyung-Joon Shin**¹. (1) School of Materials Science and Engineering, UNIST, Ulsan 44919, Korea (the Republic of) (2) School of Energy and Chemical Engineering, UNIST, Ulsan 44919, Korea (the Republic of)

Recently, monoethanolamine (MEA) coated on TiO_2 surface has drawn attention because it can lower the work function of TiO_2 effectively in photo-electronic devices such as OLED and solar cells. Increasing interest in the application of amine-based organic films as a coating material to lower the work function energy of metal oxide demands fundamental understandings of interface in the single molecular level. In this study, we examined the defect-associated adsorption of monoethanolamine on $\text{TiO}_2(110)$ surface by means of scanning tunneling microscopy and first principle

calculations. We found that the adsorption site of MEA on TiO₂(110) surface changes as a function of surface coverage. The MEA firstly adsorbs on the oxygen vacancy (O_v) of TiO₂(110) surface in a dissociated form, which is different from the previously reported result at full coverage. The hybridization of orbitals between a Ti atom and an oxygen atom of MEA attributes to the dissociative adsorption on O_v. As the MEA coverage increases, oxygen vacancies are fully occupied with the molecules and Ti rows become adsorption sites for MEA molecules. The equilibrium adsorption site varies in line with the surface coverage of TiO₂(110) surface. At high coverage, adsorption of MEA molecules on the Ti rows near O_vs is disturbed by the pre-adsorbed MEA molecules on O_vs. Our results confirm that the defects at oxide surfaces and the intermolecular interactions control the work function of the system as well as the stable configurations of adsorbates. The dissociative adsorption of MEA molecules on O_v was found to be more efficient at lowering the work function of TiO₂ surface, suggesting that defect control can be used to improve the performance of organic-inorganic hybrid systems.



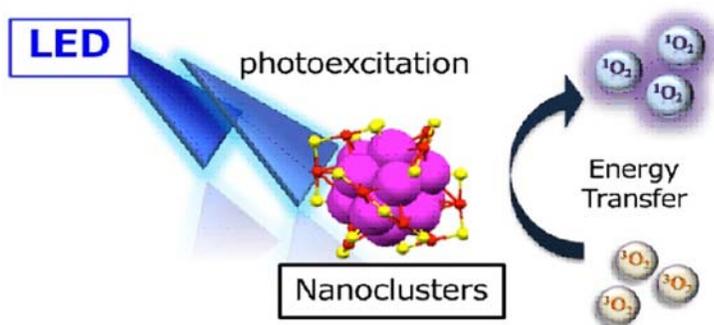
COLL 576

Aggregation/self-assembled approach for efficient AuAg bimetallic nanocluster-based photosensitizers

Hideya Kawasaki, hkawa@kansai-u.ac.jp, **Daiki Hikosou**, **Satoshi Saita**. *Kansai University, Osaka, Japan*

Recently, great efforts of thiolate-protected gold nanoclusters (Au NCs) have been devoted to the exploration of the potential diagnostic and therapeutic applications of such as biological analysis, biological imaging, therapeutic applications because of the high stability, the targeting ability by the surface modification, and the low toxicity, besides the unique physio-chemical properties. One of the therapeutic applications is a photosensitized generation of reactive oxygen species (ROS) via Au NCs as a photosensitizer for photodynamic therapy. Previously, we reported effects of size and ligand species on the ¹O₂ generation for thiolate-protected Au NCs. As for organic photosensitizers, there are extensive studies on the strategy to improve the ¹O₂ generation efficiency. Incorporation of heavy atoms into molecular structures is one of the most widely used approaches to improve the ¹O₂ generation of organic photosensitizers. More recently, aggregation-induced emission (AIE) characteristics of organic photosensitizers have emerged as enhanced fluorescence and efficient photosensitizing characteristics because of the inhibition of energy dissipation through

non-radiative pass. This motivates us to develop more efficient Au NC- photosensitizer by metal doping and AIE characteristics for therapy application. In this study, we investigated effects of metal-doping and AIE characteristic on singlet oxygen generation for glutathione-protected Au NCs. To the best of our knowledge, this is first work that silver-doping and AIE characteristic both enhance the $^1\text{O}_2$ generation of the Au NCs. The AIE accelerating AuAg bimetallic nanoclusters developed in this study have been successfully used to photodynamic therapy application.



COLL 577

Addressing the isomer cataloging problem for nanopores in two-dimensional lattices

Ananth Govind Rajan¹, ananthgr@mit.edu, Kevin Silmore¹, Jacob Swett², Daniel Blankschtein¹, Michael Strano¹. (1) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Lockheed Martin Space, Palo Alto, California, United States

Extended defects or nanopores in 2D materials, such as graphene and hexagonal boron nitride (hBN), can be used to tailor their electronic, magnetic, electrochemical, and barrier membrane properties. However, the existence of a large number of possible lattice isomers of nanopores makes their quantitative study a seemingly intractable problem, while confounding the interpretation of experimental and simulated data. Herein, we formulate an *ab initio* solution to this *Isomer Cataloging Problem (ICP)*, which combines extensive electronic-structure calculations, kinetic Monte Carlo simulations, and chemical graph theory consistent with the underlying symmetries of 2D materials, to generate a catalog of unique, most-probable isomers of 2D lattice nanopores. The calculated first-principles data set provides precise, experimentally consistent rates for transitions between nanopore shapes in the lattice, as shown for graphene. The results demonstrate remarkable agreement of our model with precise nanopore shapes observed in experimental microscopy data for graphene and show that the thermodynamic stability of a nanopore is distinct from its kinetic stability. The methodology also predicts the experimentally observed prevalence of triangular nanopores in hBN, supporting the assertion that it can solve a wide range of ICPs for other 2D membranes and lattices, thereby providing a much-needed connection between molecular design and fabrication. The methodology developed herein should

accelerate the application of nanoporous 2D materials for optoelectronics, magnetism, gas separations, desalination, and biological applications, by establishing specific links between experiment and theory/simulations through the solutions of ICPs.

COLL 578

Towards the understanding and engineering of the asymmetric electric field screening in van der Waals heterostructures

Lu Hua Li², Tian Tian¹, tian.tian@chem.ethz.ch, Qiran Cai², Chih-Jen Shih¹, Elton J. Santos³. (1) D-CHAB, ETH Zürich, Zürich, Switzerland (2) Institute for Frontier Materials, Deakin University, Geelong, Victoria, Australia (3) School of Mathematics and Physics, Queen's University Belfast, Belfast, United Kingdom

Van der Waals heterostructures (vdWH), the nanoscale Lego built by 2D materials, enable the control of material properties with numerous combinations at atomic precision. Electric field screening is one of the key characteristics governing the performance of vdWH-based devices. Here, we use a compelling set of theoretical and experimental techniques to elucidate the intrinsic screening properties of vdW heterostructures (vdWHs) formed by MoS₂ and graphene layers. Using electric force microscopy (EFM), we experimentally observed an asymmetric electric response in the MoS₂/graphene vdWHs with respect to the polarity of the external electric field. When the electrostatic potential of graphene is higher than MoS₂, the electric field is highly screened due to high density of polarized charges, while the electric field is only partially screened by reversing the polarity of the field. The asymmetric electric screening effect is thickness-dependent, in particular on the number of MoS₂ layers, while increasing graphene layer number showed smaller influence on the electric field screening properties. The cause for the asymmetric screening behaviour is further studied by multiscale simulations combining van der Waals *ab initio* density functional theory (DFT) calculations and quantum capacitance-based electrostatic model. Our theoretical simulations indicate that asymmetric dipolar contributions at the heterostructure interface are responsible for the unusual field-effect screening, which further attributes such behaviour to the energy level alignment and distinct electronic structures between graphene and MoS₂. The principles presented here can be readily applied to other type of vdWHs, which facilitate the engineering the fundamental property of screening in vdWHs, as well as optimized design of functional heterostructure devices.

COLL 579

Self-assembly of anisotropic nanocrystals and their transformations under high pressure

Ou Chen, ouchen@brown.edu. Brown University, Providence, Rhode Island, United States

Anisotropic multi-component nanocrystals, which simultaneously contain more than one type of constituents with distinct nature, are a subclass of nanocrystals with unique and promising properties. Given the dual nature inherited from individual constituents and their interactions, anisotropic multi-component nanocrystals show great promise to exhibit combined properties and synergistically enhanced functionalities. These anisotropic multi-component nanocrystals with asymmetric surfaces offer the possibility of their superiority as building blocks for self-recognized and self-regulated superstructures. In this talk, I will use the quantum dot (QD)-Au nanocrystals as a model system to discuss the anisotropic multi-component nanocrystal superstructure formation process based on both the experimental observation and molecular dynamic computer simulation. Both nanocrystal translational ordering and atomic orientation alignment will be discussed in this complicated self-assembled system. Then, I will also talk about the HNC structural and morphological transformations from atomic, nano to meso length scales using external pressure induced deviatoric stress as a novel means.

COLL 580

Silicon nanowires as an effective photoelectrode for solar-driven CO₂ reduction applications

Dunwei Wang¹, dunwei.wang@bc.edu, Wei Li¹, Da He¹, Gonghu Li². (1) Boston College, Chestnut Hill, Massachusetts, United States (2) Department of Chemistry, University of New Hampshire, Durham, New Hampshire, United States

Direct solar-driven CO₂ reduction holds great promise for mitigating greenhouse gas effect by fossil fuel usage. It also offers a direct route to high-value chemicals for further downstream chemical transformations. The key to this reaction is a photoelectrode material efficient in harvesting solar energy and convert the energy to chemical form by charge excitation, separation and transfer. We present in this talk that Si nanowires is a great platform for such applications. The electrode features the advantages of Si, including a suitable bandgap, outstanding charge separation capability and a relatively negative conduction band minimum. It also features the advantages of nanowires in that better light absorption and charge transfer are expected thanks to the nanoscale morphologies. We show in this talk that the photoelectrode is highly effective in reducing CO₂ in non-aqueous solutions for the production of alpha-carboxylic acid and CO, respectively. The importance of forming proper reaction intermediates for the desired reactions, as well as the implications of the nanoscale morphologies, will be discussed.

COLL 581

Promoting effect of Ni(OH)₂ on Pt/Pd for electrocatalytic alcohol oxidation reaction

Yanguang Li, yanguang@suda.edu.cn. Soochow University, Suzhou, China

Active and durable electrocatalysts for alcohol (methanol or ethanol) oxidation reaction are of critical importance to the commercial viability of direct alcohol fuel cell technology. Unfortunately, all current electrocatalyst materials fall far short of expectations and suffer from rapid activity degradation. In spite of tremendous efforts over the past several decades, little progress has been made in this regard. Herein, we report the remarkable promoting effect of Ni(OH)₂ on Pt or Pd nanocrystals for electrocatalytic alcohol oxidation reaction in alkaline solution. Hybrid electrocatalysts consisting of intimately mixed nanosized Pt or Pd particles, defective Ni(OH)₂ nanoflakes and a graphene support are prepared via a two-step solution method. The incorporation of highly defective nickel hydroxide nanostructures is believed to play the decisive role in promoting the dissociative adsorption of water molecules and subsequent oxidative removal of carbonaceous poison on neighboring platinum sites. As a result, the hybrids exhibit exceptional activity and durability toward efficient methanol oxidation reaction. Under periodic reactivations, the hybrids can endure at least 500,000 s with negligible activity loss, which is two to three orders of magnitude longer than all available electrocatalysts. Moreover, the incorporation of Ni(OH)₂ is also found to markedly shift the reaction selectivity from the originally predominant C2 pathway toward the more desirable C1 pathway during the ethanol oxidation even at room temperature.

COLL 582

Synthesis of hollow multimetallic nanoparticles as photo and electrochemical catalysts

Jing Zhao, jing.zhao@uconn.edu, Shutang Chen, Sravan Thota, Yongchen Wang. Chemistry, University of Connecticut, Storrs Mansfield, Connecticut, United States

Multimetallic nanoparticles are promising photo and electrochemical catalysts for many chemical reactions. In my group, we synthesized many kinds of solid and hollow Au, Pt and Pd based bimetallic and trimetallic nanoparticles of varying shapes. Galvanic replacement, thermal treatment and acid treatment have also been used to convert solid core@shell or alloy nanoparticles to hollow nanoparticles. The structural change of the nanoparticles from solid to hollow was monitored with transmission electron microscopy along with single particle scattering spectroscopy. Single particles spectroscopy revealed that the transformation of the internal structure of the nanoparticles gave rise to special spectral features in the scattering spectra of the nanoparticles. The multimetallic nanoparticles were good photo and electrochemical catalysts for reactions including p-nitrophenol reduction, methanol oxidation and oxygen reduction reactions.

COLL 583

Increasing the productivity of electrosynthesis with flow-through nanowire electrodes

Benjamin J. Wiley, *bjw24@duke.edu. Chemistry, Duke University, Hillsborough, North Carolina, United States*

Organic electrochemistry can offer a path to producing the chemicals required by society with reduced environmental harm by replacing toxic, stoichiometric oxidants and reducing agents with electricity generated from renewable energy sources, but it is not widely used on an industrial scale. One of the reasons for this is electrochemical reactors tend to be much larger than homogeneous chemical reactors for a given rate of chemical production, and thereby require greater upfront investment. The high surface area per unit volume and large mass-transfer rates offered by three-dimensional porous electrodes could potentially increase the productivity of electroorganic synthesis. This presentation will describe the characteristics of a Cu nanowire electrode that has 15 times more surface area and is 32 times more conductive than carbon paper, which currently has the highest surface area of any commercially available flow-through electrodes. The improvement in surface area is due to the small diameter of the nanowires relative to carbon fibers. The higher conductivity is due to the intrinsically higher conductivity of Cu, and the fact that the metal nanowires can be sintered together. The porosity of the nanowire electrode is 0.94, but its hydraulic permeability was 89 times lower than carbon paper. For Cu ion reduction, the Cu nanowire electrode can achieve the same single-pass conversion as carbon paper at flow rates up to 1000 times greater under mass transport-limited conditions, and 10 times greater under kinetically limited conditions. Results for the hydrogenation of furfural will also be presented.

COLL 584

Multi-shelled metal oxides hollow materials: Synthetic chemistry and applications

Dan Wang, *danwang@ipe.ac.cn. State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Acad, Beijing, China*

Multi-shelled hollow micro-/nanostructured materials possess attractive properties such as high specific surface area, low density, and high loading capacity, which endow them with potential applications in energy conversion and storage, sensors, catalysis, electromagnetic absorption and drug delivery, etc. A large number of progresses have been made on their synthesis, compositional and geometric manipulation, and applications during the past decade.

The structural complexity of the multi-shelled hollow micro-/nanostructures makes the synthesis more difficult than for single- and double-shelled ones. Our group proposed a general and widely usable sequential templating approach to prepare multi-shelled hollow spheres by utilizing carbonaceous microspheres as templates to adsorb metal ions and heating them to remove the template particle and generate hollow structures. Numerous multi-shelled hollow spheres of single metal oxides (such as α -Fe₂O₃, Co₃O₄, NiO, CuO, and ZnO), binary metal oxides (MFe₂O₄, M = Zn, Co, Ni, Cd) and also heterogeneous mixed metal oxides (ZnO@ZnO/ZnFe₂O₄@ZnO/ZnFe₂O₄) have been successfully prepared using this templating method. The concentration and radial

distribution of metal ions can be adjusted by changing the corresponding experimental conditions, such as the metal salt concentration, the solvent, the adsorption temperature and duration, the heating temperature and rate, and so forth, thus controlling the geometric parameters of the multi-shelled hollow structure products.

The breakthrough of synthetic methodologies for multi-shelled hollow micro-/nanostructures also provide opportunities to acquire unique physical or chemical properties and performance in specific applications by manipulating their geometric structures, such as shell numbers, shell size and thickness, inter-shell spacing as well as shell composition and morphology. Many successful examples have been well demonstrated in the specific fields, including dye-sensitized solar cells, lithium ion batteries, photocatalytic water splitting etc.

COLL 585

Cu-based hybrid nanocrystals for electrochemical CO₂ conversion

Raffaella Buonsanti, raffaella.buonsanti@epfl.ch. EPFL, Sion, Switzerland

Among the available methods for CO₂ conversion, the electrochemical route is a promising technology, because of the combined advantage of CO₂ utilization and production of chemicals as well as storage of renewable energies. Nevertheless, there are challenges, limiting its practical implementation, including: large overpotentials and low selectivity towards multicarbon products. Copper still remains the only suitable electrocatalyst to produce C₂/C₃ products, yet it is not active and selective enough. Breaking the scaling relations between the reaction intermediates will be key to make real breakthroughs in the field.

In this talk, I will highlight how colloidal nanocrystals can aid towards achieving this goal. We have recently showed that the material tunability afforded by colloidal chemistry allows to build unambiguous structure/properties between Cu NCs of different sizes (8nm to 60nm) and shapes (cubes and spheres) and their behaviour as electrocatalysts for CO₂ reduction. An unexpected selectivity trend was found, with 44nm nanocubes showing 40% faradaic efficiency towards ethylene, which is one of the highly desirable products. I will discuss our recent stability studies by HR-TEM and theoretical calculations, which are elucidating the mechanisms behind such a behaviour. Furthermore, the recent results on Cu-Ag dimers and alloyed nanocrystals will be presented.

COLL 586

Spherical micelle transition behaviors at different composition of calix[4]arene by the electrostatic interaction

Ji Ha Lee, aprilgem@naver.com, Shota Fujii, Rintaro Takahashi, Kazuo Sakurai. University of Kitakyushu, Fukuoka, Japan

Calix[4]arene based spherical micelles in aqueous solution form the monodispersed micellar structure. We can control the morphology transition via electrostatic interaction between head groups of calix[4]arene. Interestingly, the control of ratio of calix[4]arene were provided the variety morphology change in the cylinder from sphere to vesicle. The morphology changes were investigated small-angle X-ray scattering (SAXS), light scattering (LS), and isothermal titration calorimetry (ITC).

COLL 587

Effect of tail terminal trimethyl silyl groups on interfacial properties and aggregation behavior of surfactants

Masanobu Sagisaka¹, sagisaka@hirosaki-u.ac.jp, Kazuki Fujita¹, Takumi Endo¹, Tsuyoshi Narumi¹, Atsushi Yoshizawa¹, Adam Czajka², Julian Eastoe². (1) Hirosaki University, Hirosaki Aomori, Japan (2) University of Bristol, Bristol, United Kingdom

A fluorocarbon (FC) surfactant is the most effective and efficient surfactant to generate a low surface energy, resulting in very low aqueous surface tensions of < 25 mN/m and repellences for water and oil. However, as these compounds are typically expensive and environmentally unfriendly, a low surface energy fluorine-free surfactant comparable to a FC surfactant has been required for practical applications in chemical industries.

To develop a low surface energy fluoride-free surfactant, this study synthesized double and triple hydrocarbon-tail surfactants having tail terminal trimethylsilyl (TMS) groups (AOTSiC and TCSiC, respectively), and examined interfacial properties and aggregation behavior of those surfactants in water and/or heptane. Interestingly, TMS surfactants were found to have an excellent surface tension lowering ability in water, and to achieve very low surface tensions of 23.8-23.9 mN/m at 35 °C. The excellent surface tension lowering ability of AOTSiC was further enhanced with the optimum quantity of calcium or magnesium chloride, and it succeeded the aqueous surface tension of 21.3 mN/m. This value is similar to that of a short or middle fluorocarbon surfactant and extremely lower than for a conventional hydrocarbon surfactant (i.e. 30-40 mN/m). Small-angle neutron scattering measurements for micelles in water and reverse micelles in water/heptane mixtures found the TMS surfactants to form molecular assemblies with low curvatures compared with surfactants having tail terminal t-butyl and isopropyl groups. These results will give useful information to design a low surface energy fluorine-free surfactant.

COLL 588

Phase behavior of a stabilized surfactant/fatty acid self-assembly material

Zahra Niroobakhsh¹, niroobakhshz@umkc.edu, Robert Hickey², Andrew Belmonte^{2,3}. (1) Civil and Mechanical Engineering, University of Missouri, Kansas City, Missouri, United States (2) Materials Science and Engineering, Pennsylvania State

University, University Park, Pennsylvania, United States (3) Mathematics, Pennsylvania State University, University Park, Pennsylvania, United States

Oppositely charged surfactants have gained much attention in the fields of drug delivery, proton conductors, and cell membrane modeling. Much of the work has focused on miscible surfactant systems, where electrostatic interactions have influenced the phase behavior. Immiscible cationic-anionic surfactant systems have been less studied, but have recently been shown to stabilize oil/water mixtures via an unexpected mechanism. In our previous work, we stabilized a surfactant/fatty acid self-assembly formed at the interface between an aqueous cationic surfactant (cetylpyridinium chloride) solution and a fatty acid (oleic acid, OA). The nanostructured interface was characterized using interfacial rheology and small-angle X-ray scattering (SAXS). Here, we present the phase behavior of equilibrium bulk phases and established a ternary phase diagram for CPCI, OA and water. In the ternary diagram, we observed the formation of a gel phase at the equimolar mixing ratio of OA and CPCI similar to catanionic surfactant systems. A detailed comparison of bulk and interfacial materials characteristics is discussed. The phases of the bulk gel and the interfacial material exhibit similar viscoelastic and phase behavior, suggesting that the morphology of the interfacial gel is thermodynamically stable. The work presented here has implications in wide variety of complex fluid systems including surfactant mixtures, polymer solutions, emulsions, and colloidal domains.

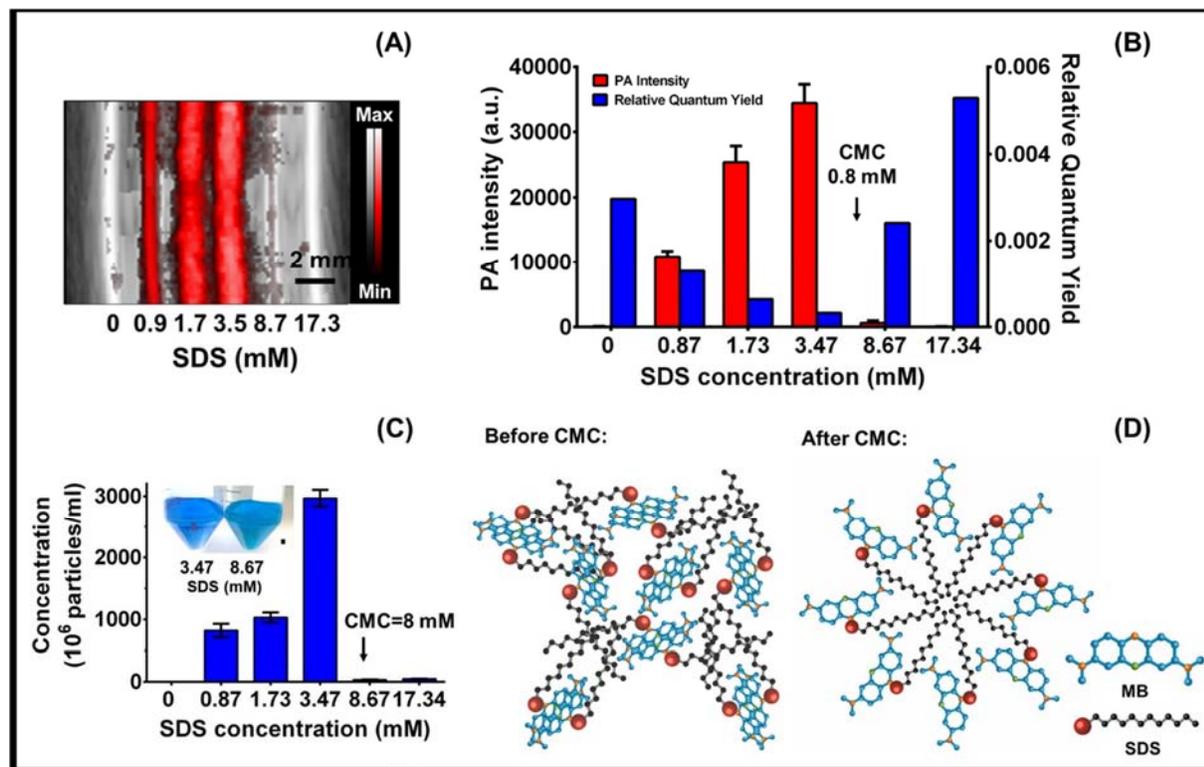
COLL 589

Switchable photoacoustic effect due to micellization of sodium dodecyl sulfate with methylene blue

Junxin Wang, junxinud@gmail.com, Ching-Yu Lin, Jesse V. Jokerst. University of California San Diego, La Jolla, California, United States

Methylene blue (MB) is an important photoacoustic contrast agent and its interaction with sodium dodecyl sulfate (SDS) is of interest because it exhibits a characteristic blue shift in the absorbance spectrum. However, the interaction details such as the binding site remained unclear. Here, we study the binding kinetic of MB and SDS using photoacoustic (PA) imaging, nanoparticle tracking analysis (NTA), and spectroscopy. We noted a 492-fold photoacoustic enhancement of 0.05 mM MB upon addition of 3.47 mM SDS and later a 54-fold decrease at a higher concentration above SDS's critical micelle concentration (CMC) at 8.67 mM (**Panel A**). The relative quantum yield of MB revealed a trend opposite to the photoacoustic intensity (**Panel B**). Meanwhile, NTA analysis indicated increasing formation of non-micellar MB-SDS clusters as SDS concentration approaching the CMC whereas the clusters disassociated at SDS concentration above the CMC (**Panel C**). These trends suggested that the fluorescence quenching and formation of MB-SDS cluster contributed to the photoacoustic enhancement. A comparison study of MB/hexadecyltrimethylammonium bromide (CTAB), MB/sodium octyl sulfate (SOS), and MB/sodium chloride (NaCl) indicated that MB interacted with the sulfate moiety of SDS before and after micellization. We

conclude that MB forms aggregates with SDS at pre-micellar concentrations and MB monomers bound to SDS at micellar concentrations (**Panel D**).



Panel A reveals the switchable photoacoustic intensity of MB with increasing concentrations of heparin. The corresponding relative quantum yield measurement and nanoparticle tracking analysis are shown in panel B and C. Panel D illustrates the form of MB-SDS aggregates at pre-micellar and micellar concentrations.

COLL 590

Magnetic surfactants as a versatile tool for functional materials design

Andreea Pasc, andreea.pasc@univ-lorraine.fr. Faculte des Sciences, University of Lorraine, Vandoeuvre les Nancy, France

Magneto-responsive surfactants are gathering increasing attention and were already use to design several molecularly organized systems such as magnetic micelles or microemulsion or to magnetize DNA. Moreover, magneto-responsive surfactants can also be used for material design. In this context, it will be firstly presented the structuring and the magnetization of hexagonally ordered mesoporous silica.

Then, it will be shown that magneto-responsive surfactants combined with solid lipid nanoparticles (SLNs) can be used as colloidal tools for meso-macroporous supported catalyst. The key point of this work is that the size of iron oxide nanoparticles embedded in the meso-macroporous matrices has been decreased to 15–20 nm in diameter to

give high surface area of the active catalytic sites in comparison with the previous submicron sized iron oxide. As a matter of fact, the resulting material exhibits an excellent performance in a Fenton-like reaction for methylene blue degradation, even at low amount of iron oxide.

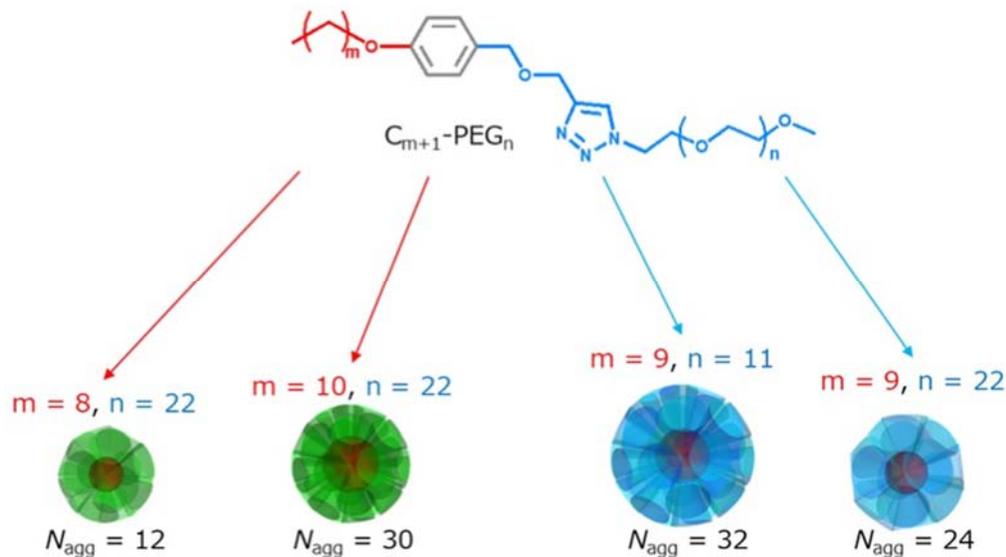
Finally, a novel system of paramagnetic vesicles was designed using ion pairs of iron-containing magnetic surfactants. Unilamellar vesicles (diameter ~200 nm) formed spontaneously and were characterized by cryogenic transmission electron microscopy, nanoparticle tracking analysis, light and small-angle neutron scattering. Moreover, for the first time, it is shown that magnetization measurements can be used to investigate self-assembly of such functionalized systems, giving information on the vesicle compositions and distribution of surfactants between the bilayers and the aqueous bulk.

COLL 591

Monodispersity of the micelles composed of polyethylene glycol (PEG)-attached surfactants: Platonic micelles in conventional micelle system

Hayata Matsumoto, y7mab009@eng.kitakyu-u.ac.jp, Shota Fujii, Rintaro Takahashi, Kazuo Sakurai. University of Kitakyushu, Fukuoka, Japan

According to the thermodynamic description of micellar formation, micelles always have a distribution in their aggregation number (N_{agg}). However, we have recently discovered that some calix[4]arene-based surfactants self-assemble into completely monodisperse micelles in terms of N_{agg} . Interestingly, the N_{agg} s are always consistent with the vertex number of Platonic solids, indicating the formation of polyhedral structures. Then, we named them Platonic micelles. The thermodynamic consideration for the formation of Platonic micelles, which we proposed, suggests that these special properties would be occurred in the system of conventional micelles without calix[4]arene building blocks. To construct Platonic micelles, the micellar N_{agg} should be small (< 30), which can be achieved by increasing the interfacial area (a_e) between hydrophobic and hydrophilic domains. In this study, we have designed and synthesized surfactants bearing polyethylene glycol (PEG) to confer large a_e and investigated their aggregation behavior using small angle scattering techniques.



COLL 592

Structural and rheological properties of micelles in a shear flow

Breannan O Conchuir¹, conchsb@tcd.ie, Richard L. Anderson², Michael A. Johnston³. (1) IBM Research UK, Warrington, United Kingdom (2) STFC Hartree Centre, Warrington, United Kingdom (3) IBM Research Ireland, Dublin, Ireland

The viscosity of surfactant solutions is of vital interest to the industrial sector. However, the geometric and rheological properties of micellar suspensions remain poorly resolved, especially when the system is stressed by an external shearing force. As a result, companies are beginning to turn towards computer aided formulation to better understand and optimise the rheological properties of their products, from the tactile characteristics of personal-care products, to the action of engine lubricants.

In this talk, we will present the results of our coarse-grained Dissipative Particle Dynamics (DPD) DL-MESO simulations of various industrial surfactant systems in shearing flows. These computations elucidate the delicate interplay between force field parameters, structures and rheology. The threefold relationship between a) surfactant interactions and concentration, b) micelle formation, size, shape and orientation, and c) system shearing stress, shear rate and viscosity, is extensively explored in this study. The calculations were performed on IBM power-based High Performance Computing (HPC) systems and the DPD force field interaction parameters were generated using automated optimization methods.

COLL 593

Formation of ultra-uniform micelles via morphological evolution during a chemical reaction

William R. Lindemann, *wlindemann6@gmail.com*, Jia Tian, Julia Ortony. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

In self-assembled systems, structural transitions are frequently driven by changes in solution conditions such as pH, temperature, and salt concentration. Much rarer are transitions driven by steric changes in the molecule caused by chemical reactions. In our recent work, we created a series of novel, self-assembling amphiphiles designed to photo-catalyze reactions for fuel production. Upon self-assembly in water, these molecules initially adopt a cylindrical geometry. However, after undergoing a chemical reaction at their surface, these nanostructures transform into extremely uniform micelles with a maximum size variation of ~7%. Herein, we provide TEM, cryo-EM and SAXS evidence for the uniformity of these micelles, as well as observations of morphological evolution during the transition process. We speculate that this unique phenomenon occurs by a Rayleigh decomposition process, which explains the unusually high regularity of the micelles observed.

COLL 594

Branched pseudo-oligomeric cationic surfactant in organic media

Marc A. Walters, *marc.walters@nyu.edu*, Bryan Jin, Leslie Vogt-Maranto, Ariel Velasquez. Chemistry, New York University, New York, New York, United States

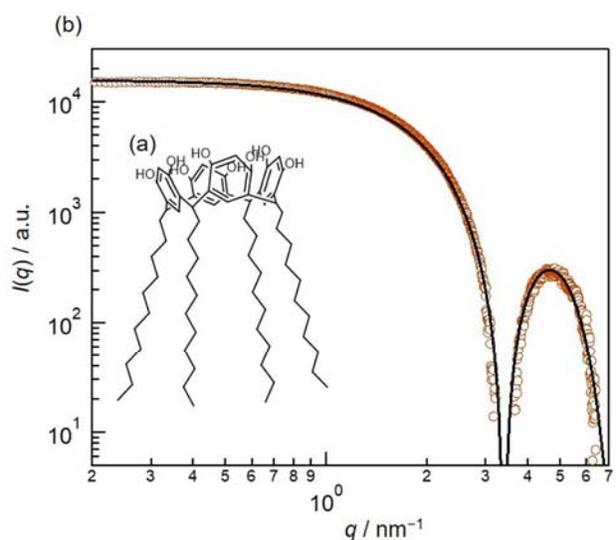
Cetyldimethylamine (CDAm) was combined with diethylenetriaminepentaacetic acid (DTPAH₅) to form a supramolecular amphiphile (SA) formally designated as (CDAmH)₅[DTPA]. The supraamphiphile dissolves in chloroform to form reverse micelles (RMs) that convert to vesicles with increasing amphiphile concentration. The spatial extent of a single SA, estimated by density functional theory optimizations, indicates that the observed particles are consistent with lamellar aggregates. Particle size varies as a function of SA concentration and is consistent with the extension of surfactant tails in opposite directions away from the region of head group-DTPA interaction. Further, spectroscopic evidence shows that the SA forms as a result of proton transfer. The DTPA⁵⁻ anion reacts with FeCl₃ in chloroform to produce micron scale particles. These iron containing particles have been characterized by scanning electron microscopy and show a relatively uniform distribution of iron in the particle core.

COLL 595

Platonic micelles part 1: Monodisperse micelles in the system of reverse micelles

Shota Fujii¹, *s-fujii@kitakyu-u.ac.jp*, Rika Miyake¹, Ji Ha Lee¹, Rintaro Takahashi³, Kazuo Sakurai². (1) The University of Kitakyushu, Kitakyushu, Japan (2) U of Kitakyushu Dept of Chem, Kitakyushu Fukuoka, Japan

We have recently discovered that some calix[4]arene-based amphiphiles self-assemble into completely monodisperse micelles in terms of the aggregation number (N_{agg}). Interestingly, the N_{agg} s are always consistent with the vertex number of Platonic solids, indicating the formation of polyhedral structures. Thus, we name them Platonic micelles. Regarding the thermodynamics of the formation of Platonic micelles, the micelles would be formed in the system of reverse micelles. Undecylcalix[4]resorcinarene, whose building block structure is very similar to calix[4]arene, self-assembles into small spherical micelles in organic solvent including toluene and chloroform. The small angle X-ray scattering (SAXS) profile of the micelle in toluene displayed a sharp minimum at $q = 3.5 \text{ nm}^{-1}$, indicating the monodispersity of the micelles in terms of the size as well as the molar mass. In this study, we have also characterized the thermo-responsiveness in the micellar structure using small angle scattering techniques.



(a) Chemical structure of Undecylcalix[4]resorcinarene.
 (b) SAXS profile of the reverse micelle composed of Undecyl-calix[4]resorcinarene in toluene (red points) and fitting curve calculated using spherical model (black solid line).

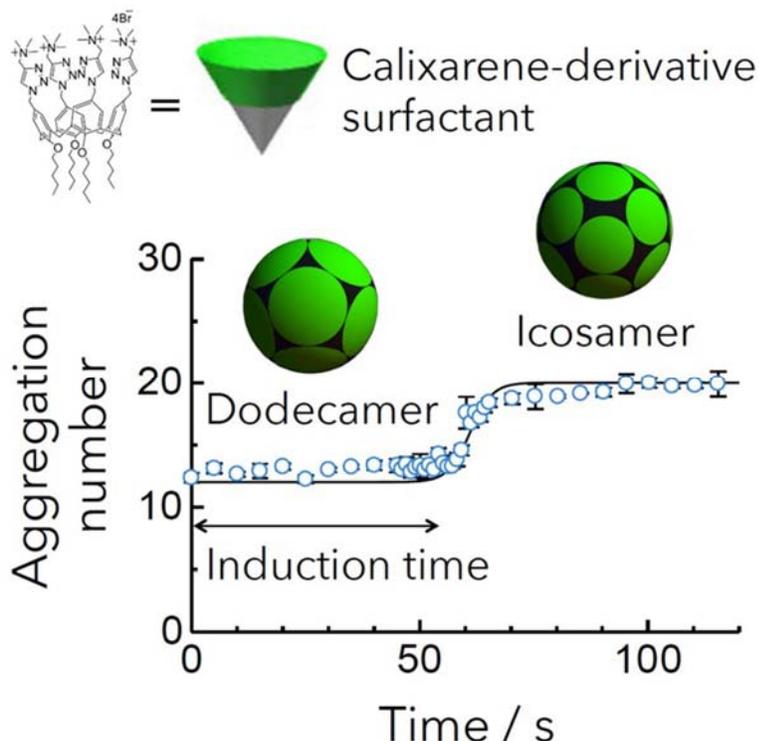
COLL 596

Platonic micelles part 2: Kinetic consideration of the micelles with the discrete aggregation numbers and mono-dispersity

Kazuo Sakurai², Rintaro Takahashi³, Ji Ha Lee⁴, **Shota Fujii¹**, s-fujii@kitakyu-u.ac.jp. (2) U of Kitakyushu Dept of Chem, Kitakyushu Fukuoka, Japan (3) The University of Kitakyushu, Kitakyushu, Japan

Calix[4]arene-derivative surfactants form monodisperse micelles with a well defined aggregation number (N_{agg}), the value of which is selected from among 4, 6, 8, 12, and 20, corresponding to the Platonic solids. This feature is in strong contrast to conventional micelles. Here, we focused on a kinetics; a transition from dodecamer

($N_{agg} = 12$) to icosamer ($N_{agg} = 20$) induced by a rapid increase of the NaCl concentration (C_{NaCl}) using a stopped-flow device was directly observed with time-resolved small-angle X-ray scattering. N_{agg} was unchanged during 60 s after C_{NaCl} increased, and then abruptly increased to 20. This phenomenon is similar to the phase transitions in a supersaturated or supercooled state, or highly cooperative phenomena. The phenomena may be related to our hypothesis that only a few N_{agg} values are thermodynamically allowed, when N_{agg} is sufficiently small. This is the first observation of such abnormal discontinuous change in micellar aggregation behavior.



COLL 597

Protein-like polymers as peptide, small molecule and protein delivery agents to cells and tissues

Nathan C. Gianneschi, ngianneschi@ucsd.edu. Chem M/C 0343, University of California, San Diego, La Jolla, California, United States

We present a strategy for packaging peptides as side-chains in high-density brush polymers as responsive, or proteolytically resistant materials. For this globular protein-like polymer (PLP) formulation, therapeutic peptides were shown to resist proteolytic degradation, enter cells efficiently and maintain biological function. In this presentation we describe the behavior of this class of peptide-polymer conjugate in the development of responsive materials for associating and entering diseased tissues and cells in vitro and in vivo. We will describe a general synthetic strategy for preparing globular like

single polymer particles, and more traditional micellar particles capable of peptide, protein and small molecule delivery to cells and tissues.

COLL 598

Bioelectronics communication: Encoding regulatory responses using nanostructured semiconductor thin films

Albena Ivanisevic, ivanisevic@ncsu.edu. North Carolina State University, Raleigh, North Carolina, United States

The talk will highlight representative studies, challenges and opportunities towards utilization of charge, conductivity, photoconductivity, polarity and surface chemistry in biomolecular interfaces.

The talk will explore how GaN, GaOOH and Ga₂O₃ nanostructured materials can be used to encode and decode physiological responses during *in vitro* studies. The semiconductor materials can be functionalized with different surface chemistries and characterized via X-ray Photoelectron Spectroscopy, Photocurrent Measurements, Atomic Force Microscopy and Kelvin Probe Force Microscopy. UV light can be utilized to induce persistent photoconductivity that results in charge accumulation on the surface. The morphological, chemical and electronic properties of the nanostructured films can be employed to activate the cell wall integrity pathway or stimulate cells. The encoded cell responses are induced by the semiconductor interfacial properties associated with the surface chemistry, nanoscale topography and the accumulation of charge on the surface that promotes the build-up of oxygen species. The semiconductor interfaces can also alter the membrane voltage of cells or the amount of intracellular calcium produced. The results thus define a strategy for bioelectronics communication where the roughness, surface chemistry and charge of the wide band gap semiconductor's thin film surface initiate the encoding of the cell response.

COLL 599

Interfacial chemistry of biomimetic asymmetric nanochannels

Liping Wen, wen@mail.ipc.ac.cn. Technical Institute of Physics and Chemistry, CAS, Beijing, China

Learning from nature has inspired the creation of intelligent devices to meet the increasing needs of the advanced community and also to better understand how to imitate biology. As one of biomimetic nanodevices, nanochannels or nanopores aroused particular interest because of their potential applications in nanofluidic devices, biosensing, filtration, and energy conversions. Here, by manipulating and modifying the surface of the artificial nanochannels, we developed some biomimetic smart nanochannels for practical applications, such as energy conversion, bioinspired photo-driven ion pump. Such applications with biomimetic nanochannels can not only help

people to know and understand the living processes in nature, but also inspire scientists to study and develop novel nanodevices with better performance for the mankind.

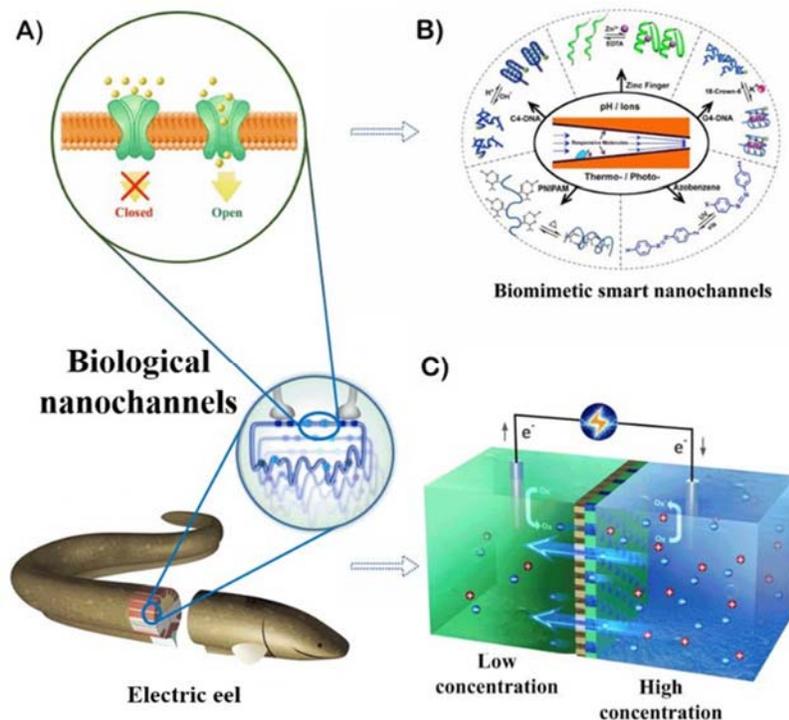


Figure 1. A) Biological nanochannels. Nanochannels in electric eel for discharging. B) Biomimetic smart nanochannels. C) Nanochannels based membrane for salinity gradient energy generation

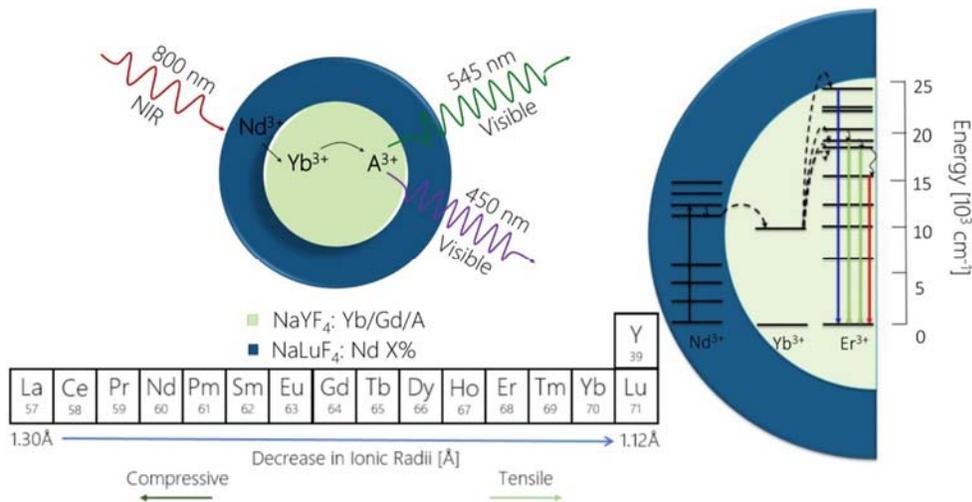
COLL 600

Concentric Nd(III)-sensitized core-shell upconversion nanoparticles for excitation with a biobeneficial wavelength

*Carina Arboleda*¹, *carboled@eng.ucsd.edu*, *Sha He*¹, *Alexandra Stubelius*², *Noah Johnson*², *Adah Almutairi*². (1) Nanoengineering, University of California San Diego, La Jolla, California, United States (2) Pharmaceutical Sciences MC 0600, University of California San Diego, La Jolla, California, United States

Ytterbium (Yb³⁺) is the ubiquitous sensitizer in lanthanide-based upconverting nanoparticles (UCNPs) and has prevailed due to the efficient energy transfer of the dopant to activator ions. However, Yb³⁺-sensitized UCNPs suffer from 980 nm absorption overlap with water —the most abundant near infrared (NIR) light absorber in the body leaving these UC processes at an inherent disadvantage for biological applications. Substitution of Yb³⁺ for Neodymium (Nd³⁺) as the sensitizing component shifts absorption to 800 nm to effectively minimize signal attenuation and reduce detrimental overheating in biological tissues. Previous reports have successfully achieved Nd³⁺-sensitization in core-shell nanostructures but they were limited to low

doping concentrations and lacked UC efficiency partly due to lattice distortions in heavily doped nanostructures. Herein we report highly doped Nd^{3+} -sensitized core-shells (CSs) that effectively relieve strain between the core and shell to achieve enhanced UC emission and structural superiority. We synthesized NaYF_4 : Yb/Gd/Er and NaYF_4 : Yb/Gd/Tm cores with NaLuF_4 shells of varied Nd^{3+} concentrations (0-50 mol%). Our highly tunable epitaxial growth method featuring a tensile-strained Lutetium (Lu^{3+}) shell facilitated remarkably higher Nd^{3+} dopant concentrations and thicker shells to ensure spatially separated Nd^{3+} . UC emission significantly increased as the Nd^{3+} shell concentration increased from 0 to 50% and Nd^{3+} concentration was successfully tuned to achieve relatively high UC efficiency. 50% Nd^{3+} doping concentration provided UC enhancements of up to 13 times compared to CS without Nd in the shell, independent of the activator. To highlight the importance of creating a tensile-strained shell of Lu^{3+} to form concentric heavily-doped shells, we synthesized compressively-strained shells of Gadolinium (Gd^{3+}) and Yttrium (Y^{3+}). Lu^{3+} shells outperformed Gd^{3+} and Y^{3+} shells in terms of UC enhancement. Cell cytotoxicity studies show PEGylated UCNPs were non-toxic and tolerable up to concentrations of 60 $\mu\text{g/ml}$; further demonstrating the potential of our UCNPs for bioimaging.



COLL 601

Target-specific glucose-conjugated gold nanoclusters as fluorescent probes for quantitative analysis of glucose metabolic cleavage in glucose transporters overexpressed cancer cells

Tsung-Rong Kuo¹, trkuo@tmu.edu.tw, **Xi-Yu Pan**¹, **Ting-Kuang Chang**², **Kuan Chen**², **Jui Chi Kuo**², **Shih-Hua Tan**². (1) Graduate Institute of Nanomedicine and Medical Engineering, College of Biomedical Engineering, Taipei Medical University, Taipei, Taiwan (2) School of Biomedical Engineering, College of Biomedical Engineering, Taipei Medical University, Taipei, Taiwan

The glucose metabolism rate in cancer cells is a crucial piece of information for the cancer aggressiveness. A feasible method to monitor processes of oncogenic mutations has been demonstrated in this work. Herein, the fluorescent gold nanoclusters conjugated with glucose (glucose-AuNCs) were successfully developed as a cancer-targeting probe for glucose transporters overexpressed by U-87 MG cancer cells, which can be observed under confocal microscopy. The glucose metabolic cleavage of glucose-AuNCs by glycolytic enzymes from U-87 MG cancer cell was measured by fluorescence change of glucose-AuNCs. The fluorescence change based on the integrated area under fluorescence spectra (A_t) of glucose-AuNCs was plotted as a function of different reaction time (t) with glycolytic enzymes. The fitted curve of A_t versus t based on the first-order kinetics was the most appropriate one to describe the mechanism of glucose metabolic cleavage of glucose-AuNCs by glycolytic enzymes. The rate constant k could be utilized to determine the glucose metabolism rate of glucose-AuNCs for the quantitative analysis of cancer aggressiveness. Our work provides a practical application of target-specific glucose-AuNCs as a fluorescence probe to analyze the glucose metabolism in glucose transporters overexpressed cancer cells.

COLL 602

Eradication of multidrug-resistant bacteria by DNA-encapsulated two-dimensional transition metal dichalcogenides

Abhishek. Debnath, adebnath@asu.edu, Sanchari Saha, Ahmed Yousaf, Alexander Green. Arizona State University, Tempe, Arizona, United States

Two-dimensional transition metal dichalcogenides (TMDCs) have been widely explored for a range of biomedical applications. Previous reports on solution-phase processing of TMDCs have relied on aggressive lithiation treatments, which require toxic chemicals and in turn hamper their use in biological systems, or have required amphiphilic surfactants to encapsulate the hydrophobic TMDCs, which can reduce biocompatibility. To overcome these problems, we have developed a novel biopolymer-based strategy for solution-phase processing of TMDCs that employs short synthetic single-stranded DNAs (ssDNAs) to stably encapsulate TMDC nanosheets in aqueous solution. ssDNA-assisted exfoliation yields TMDC dispersions with concentrations up to 1 mg/mL, significantly higher than previously reported biocompatible dispersion agents, and enables a variety of functional chemical moieties to be attached to the TMDC surface through versatile synthetic DNA chemistries, which we exploit to tether proteins to MoS₂. While the ssDNA-encapsulated TMDCs exhibit no cytotoxicity against human cell lines at concentrations up to 0.25 mg/mL, we find that the TMDC-ssDNA preparations exhibit exceptionally strong bactericidal activity against both gram-positive and gram-negative bacteria. Antibacterial assays of MoSe₂-ssDNA demonstrate 3.4 orders of magnitude higher killing of both gram-positive and gram-negative bacteria compared to graphene oxide, the most widely investigated antibacterial two-dimensional material. Moreover, we find that the use of short synthetic ssDNAs to encapsulate the MoSe₂, rather than bulky biocompatible polymers or double-stranded DNA coatings, enhances

their antibacterial activity by over an order of magnitude. Further tests of MoSe₂-ssDNA against strains of multidrug resistant bacteria, including a gram-negative “superbug” strain *Escherichia coli* resistant to 30 antibiotics and a gram-positive MRSA strain, show complete eradication of the bacteria at concentrations of 150 µg/ml and 80 µg/ml, respectively. Mechanistic investigations of bacteria treated with MoSe₂-ssDNA using scanning electron microscopy and transmission electron microscopy reveal that direct physical interactions of the bacteria with the sharp edges of the MoSe₂-ssDNA nanosheets cause breakdown of the cell envelope and are responsible for cell death. ssDNA-encapsulated TMDCs thus represent promising new materials for combating drug-resistant bacterial infections.

COLL 603

Excellent activity of biocompatible transition metal dichalcogenide nanosheets for scavenging reactive oxygen species

*DaBin Yim*¹, dabinyim@naver.com, *Ji Eun Kim*², *Hye-In Kim*¹, *Jin Kyoung Yang*¹, *Tae Woog Kang*¹, *Sun-Young Yoo*², *Jong-Ho Kim*¹. (1) Chem Eng, Hanyang Univ, Ansan Gyeonggi-do, Korea (the Republic of) (2) Hanyang university, Ansan, Korea (the Republic of)

As reactive oxygen species (ROS) display paradoxical functions depending on their concentration in biological systems, it is desired to effectively regulate them in our body. We present an approach for the simultaneous exfoliation and functionalization of transition metal dichalcogenide (TMD) nanosheets using diblock copolymers, poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) (PCL-*b*-PEG), in an aqueous solution, and their application for scavenging ROS in living cells. The three different diblock copolymers with a different length of PCL were employed to modulate the hydrophobic interaction between TMDs and the copolymers in the exfoliation and functionalization process in water. The PCL₄₆₀-*b*-PEG₅₀₀₀ showed the best exfoliation and functionalization efficiency for all the TMDs. As-prepared TMD nanosheets functionalized with the PCL₄₆₀-*b*-PEG₅₀₀₀ copolymer exhibited excellent antioxidant activities for superoxide, hydroxyl, and ABTS radicals. However, each TMD showed a unique tendency in the ROS scavenging activity: the WSe₂ nanosheets were most effective for scavenging ABTS radicals. The WS₂ nanosheets showed the best scavenging activity for hydroxyl radicals, and the MoSe₂ nanosheets displayed the most effective scavenging activity for superoxide radical. The mechanism responsible for the effective ROS scavenging by the functionalized TMD nanosheets was investigated. Finally, the TMD nanosheets were successfully applied to the scavenging of ROS in human keratinocytes cells with excellent biocompatibility.

COLL 604

Identification of dynamic domains for ligand on monolayer-grafted nanoparticles and their implications for bio-interactions

Delyan Hristov³, hristovdr@gmail.com, **Hender Lopez**^{4,5}, **Yannick Ortin**¹, **Kate O'Sullivan**¹, **Kimberly Hamad-Schifferli**³, **Kenneth A. Dawson**², **Dermot Brougham**¹. (1) School of Chemistry, University College Dublin, Dublin, Ireland (2) CBNI at School of Chemistry, University College Dublin, Dublin, Ireland (3) Engineering, University of Massachusetts Boston, Boston, Massachusetts, United States (4) Institut für Angewandte Physik, Eberhard Karls Universität Tübingen, Tübingen, Germany (5) Institut Laue-Langevin, Grenoble, France

Surface ligands play a critical role in maintaining colloidal stability of nanoparticles in high salinity media and in influencing their interaction with biomolecules a process which largely determines their biological fate. Polyethylene glycol (PEG) in particular has been a popular tool for improving particle stability, managing biomolecule surface adsorption and directing biodistribution. Recent studies have suggested that PEG grafting leads not only a reduction of protein adsorption but also the enrichment of specific entities on the surface which in turn influence response in biological environments. Detailed studies into the corona; its content, and its mechanism and timescale of formation have been conducted. It is also known that factors which can be controlled such as ligand chemistry, structure and surface coverage play a significant role not only in corona formation but also, as has been recently shown, in the functionality of proteins grafted onto the particle – ligand complex. However, there is no clear molecular understanding into graft conformation and dynamics and how they influence the key early interactions when particles are placed in a biological environment.

In this work we present a ¹H nuclear magnetic resonance (NMR) study into PEG-grafted SiO₂ NPs in D₂O suspension. By studying a library of particles of varied size, ligand coverage and graft chain length we can identify three distinct populations of monomer units, classified by their dynamics. Component **A** is rapidly moving and isotropic, similar to free PEG and is ascribed to the part of the chain furthest from the graft; restrictions closer to the surface render Component **B** slow moving on the NMR timescale; while Component **C** is 'solid-like' on the NMR timescale being broadened into the background. Spectral analysis enables quantification of the components, hence it has been demonstrated that monomer units transition between the components on activation by increasing temperature or coverage. It was also possible to determine that the observed effects are homogenous, i.e. mostly the result of In ongoing work the effect of chain disruptors, other NP types and bio-molecules, on dynamic grafted chain populations are being studied.

COLL 605

Targeting bacteria with nanoantibiotics

Mingdi Yan, mingdi_yan@uml.edu. Dept of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States

The increasing prevalence of resistance to the majority of existing antibiotics has generated a pressing global healthcare crisis. Certain highly resistant bacteria have

acquired multiple mechanisms against all available antibiotics including the drugs of last resort. New strategies are needed to combat the spreading of antimicrobial resistance. Pure nanoantibiotics (PNAs) are nanoparticles made entirely of pure antibiotic molecules. Because PNA is carrier-free, the drug encapsulation efficiency is close to 100%. Drugs presented in the nanoparticle form have also shown to inhibit resistance development by disarming the efflux pump and increasing the intracellular drug accumulation. We are developing methods for the synthesis and fabrication of PNAs. In one example, we developed a modular synthesis of fluoroquinolone derivatives and fabricated them into theranostic nanoantibiotics. These compounds readily assembled into nanoparticles that displayed enhanced luminescence. In addition, the PNAs exhibited more than an order of magnitude enhancement in the antibacterial activity compared to the soluble drugs.

COLL 606

Atomistic modeling of nanoparticles nanomedicines: From protein corona to bio-activity

Petr Kral, pkral@uic.edu. University Illinois Chicago, Chicago, Illinois, United States

We use molecular dynamics simulations to model different aspects of nanoparticles nanomedicines. First, we address the problem of peptide and protein binding to such nanoparticles. For example, we show that PEGylated micelles tend to disintegrate in the presence of protein corona, where more compact micelles with dendritic monomers are less susceptible to protein corona formation and disintegration than those with linear monomers. Second, we investigate disintegration of viruses by virucidal nanoparticles and related macromolecules, and show that these processes are very sensitive to the structures of ligands and nanoparticles, due to a highly specific multivalent binding. Finally, we discuss a bio-activity of precisely functionalized Boron clusters which can act polysaccharides, peptides, and other cellular components.

COLL 607

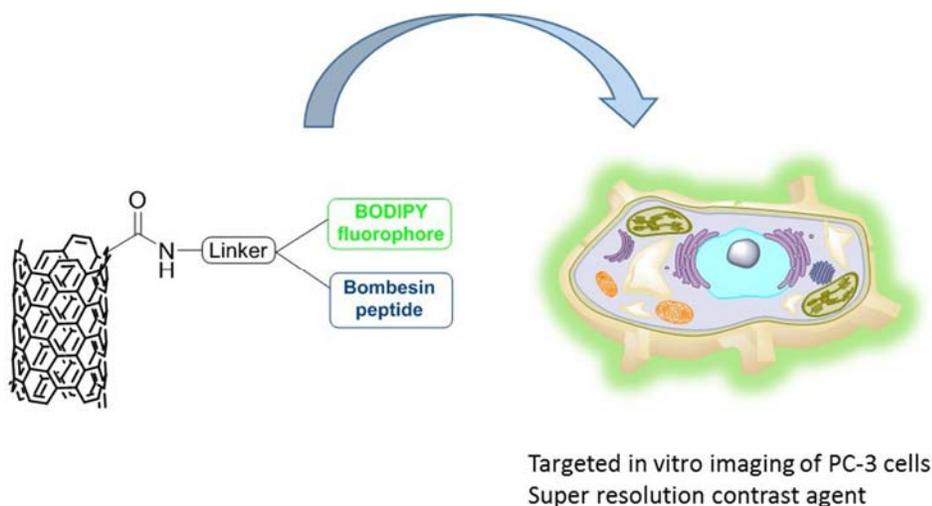
Biocompatible nanoprobe based on functionalized single-walled carbon nanotubes for the targeted imaging of prostate cancer cells

Fernando Cortezon-Tamarit¹, fctc20@bath.ac.uk, Vincenzo Mirabello¹, Haobo Ge¹, Sofia Pascu². (1) Department of Chemistry, University of Bath, Bath, United Kingdom (2) Univ of Bath, Bath, United Kingdom

Prostate cancer is the second most common cancer and one of the principal causes of mortality among men. The targeted imaging of prostate cancer has consequently attracted much interest as it allows for the detection and delineation of prostate cancer tumors. The use of carbon nanomaterials in biomedical imaging offer significant advantages such as the large surface area and ability to enter into cells.

We have developed an optical imaging nanoprobe based on single-walled carbon nanotubes (SWNT) functionalized covalently following two different strategies. Aliphatic linkers were introduced in order to improve the stability of the nanomaterial in solution and to reduce cytotoxicity when compared to pristine SWNT as demonstrated by MTT assays in PC-3 prostate cancer cells. A bifunctional BODIPY fluorophore was synthesized and conjugated to the targeting peptide fragment [7-13]-bombesin, specific for gastrin-releasing peptide receptors which are overexpressed in prostate cancer cells. The conjugate was incorporated in the nanoprobe covalently by amide chemistry.

The molecular probes and nanoprobe were characterized in detail and the behavior *in vitro* in living prostate cancer PC-3 and LNCaP cells evaluated by single-photon confocal microscopy. Furthermore, the nanoprobe was studied by other photophysical techniques such as fluorescence lifetime imaging (FLIM) and different super resolution confocal microscopy techniques (e.g. iSIM, STORM). The results indicate that the conjugate effectively targets prostate cancer cells and the nanoprobe results in a good platform for the optical imaging of prostate cancer. The nanoprobe also proved successful as a contrast agent for some of the super resolution microscopy techniques.



COLL 608

Polymer corona phase on single walled carbon nanotubes as an artificial molecular recognition site for real-time small therapeutic detection

Juyao Dong¹, juyao@mit.edu, **Michael Strano**². (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Chemical Engineering, 66-566, MIT, Cambridge, Massachusetts, United States

Label-free sensors based on nanomaterials are capable of real-time, continuous monitoring of target biomolecules. However, most of current methods focus on

electronic and mechanical sensors, which are based on surface substrates that are limited for in situ use. Label-free detection based on optical signals are hence designed to tackle these problems. Single walled carbon nanotubes are ideal optical signal transducer as their near infrared fluorescence is highly sensitive to the dielectric environment. In addition, the nanoparticle surface serves as a scaffold for constructing an artificial molecular recognition site, composed of amphiphilic polymer formed corona phase on nanotube surfaces. The resulting three-dimensional configuration binds to Vardenafil with high specificity and affinity, and transduces the recognition events via the modulated fluorescence of nanotubes. The recognition conformation depends highly on the monomer structure, the composition ratio and the length of polymers. Our results thus demonstrate an optical nanosensor that integrates an artificial recognition site on nanoparticle surface for in situ, continuous monitor of small therapeutics.

COLL 609

Effects of surface atom coordination on protein-nanoparticle interactions

Zehui Xia¹, xiazehui0901@gmail.com, **Esteban Villarreal**², **Hui Wang**², **Boris Lau**³. (1) *Civil and Environmental Engineering, University of Massachusetts Amherst, Sunderland, Massachusetts, United States* (2) *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina, United States* (3) *University of Massachusetts Amherst, Amherst, Massachusetts, United States*

The biological activity of nanoparticles (NPs) has been demonstrated to be shape dependent. This is resulted from the difference in surface energetics of various crystal facets arising from different portions of edges, corners and surface defects. Here we studied how surface atom coordination impacts the adsorption of proteins (Beta-lactoglobulin, BLG) onto selectively synthesized Au quasi-spherical nanoparticles (QSNPs) and surface-roughened nanoparticles (SRNPs) of similar diameters (~150 nm). The surface of QSNPs are mainly enclosed by {100} and {111} facets covered with close-packed Au atoms, whereas SRNPs are enclosed by a mixture of undercoordinated and close-packed surface atoms at the highly curved and locally flat surface regions.

Protein adsorption kinetics and conformation changes at various number ratios of BLG:NP were monitored by UV-Vis spectrophotometry, dynamic light scattering, and circular dichroism spectroscopy. At low number ratios, when NP surfaces are partially covered, BLG-SRNPs exhibited greater conformational changes with a significant increase in beta-sheet content and decrease in alpha-helix content. There was negligible change in UV-Vis peak position/height and hydrodynamic diameters (H_D) for both BLG-SRNPs and BLG-QSNPs. However, at a number ratio > 300, the UV-Vis peak position/height and H_D of BLG-SRNPs started to increase. This seems to suggest that the aggregation of BLG-SRNPs was induced by the increasing amount of denatured BLG. BLG-QSNPs exhibited similar aggregation behaviors at a number ratio >5,000. We propose that the notable difference in the adsorption of BLG onto SRNPs and QSNPs are due to the effects of surface atom coordination. Since the undercoordinated surface Au atoms are more reactive than the close-packed surface atoms, a lower

number ratio is needed to induce the denaturation of adsorbed BLG and the subsequent aggregation. These findings are important in improving our understanding of the possible role of surface atom coordination in the formation and conformation of protein corona.

COLL 610

Polymeric surface chemistry for quantum dot-based pH imaging

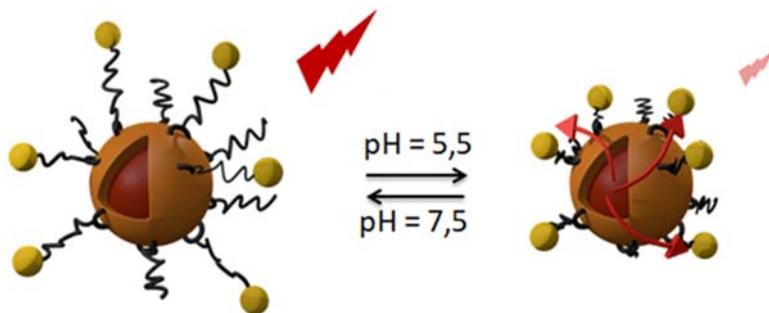
Manon Debayle¹, manon.debayle@espci.fr, **Nicolas Lequeux**², **Thomas Pons**³. (1) Chemistry, ESPCI, Paris, France (2) LPEM, ESPCI-Paris France, Paris, France (3) LPEM, ESPCI, Paris, France

Intra and extra-cellular pH are key factors in many biological and physiological processes. For example, the slightly lower extracellular pH in tumor micro-environments has a strong impact on tumor growth and drug delivery. Noninvasive *in vivo* pH imaging would therefore improve our understanding of the intra-tumoral pH regulation and its effects. Colloidal quantum dots (QDs) are interesting fluorescent probe candidates for *in vivo* pH imaging, thanks to their high quantum yield, adjustable emission and high photostability.

We have designed a novel copolymeric QD surface ligand composed of dithiolane and sulfamethazine moieties. Reduced dithiolanes act as anchoring groups to the QD surface, while sulfamethazine provide pH-sensitivity through reversible protonation/deprotonation. Binding of peripheral gold nanoparticles (GNP) around the central QD is achieved using remaining dithiolanes. Neutralization of the sulfamethazine moieties at acidic pH causes shrinking of the polymer ligand shell and a concomitant decrease in QD-GNPs separation distance. Since GNPs are able to quench the QD fluorescence by non-radiative energy transfer with a highly distance-dependent efficiency, this pH-sensitive conformation change leads to a strong modulation of the QD fluorescence signal.

We show that under physiological conditions, sulfamethazine polymer ligands enable a transition around pH 6, which is well adapted to the study of biological systems and this modulation is fully reversible within the physiological pH range (pH 5,5-8).

In order to provide robust pH imaging, we propose two different ratiometric measurements, based either on QD fluorescence lifetimes or on ratiometric measurements of two QD populations functionalized with pH-sensitive or pH-insensitive surface chemistries, respectively. Finally, we integrate these probes in the cytoplasm of red blood cells to enhance their circulation lifetime in the blood stream. These probes remain functional and sensitive to extracellular pH. This polymeric surface chemistry is versatile and adaptable to any type of QDs, opening interesting possibilities for *in vivo* pH imaging in tumors or other tissues.



QD coated by pH sensitive polymeric ligands end-functionalized with gold nanoparticles

COLL 611

Cellular delivery of doxorubicin mediated by disulfide reduction of a peptide-dendrimer bioconjugate

Kelly Burns¹, kburns929@gmail.com, **James Delehanty**². (1) Center for Biomolecular Science and Engineering, US Naval Research Laboratory, Davidsonville, Maryland, United States (2) US Naval Research Lab, Washington, District of Columbia, United States

The main goals of peptide-mediated drug delivery are the targeting of therapeutics to diseased tissues coupled with the controlled intracellular release of the drug cargo. Specific targeting of cancerous cells is often aimed at cancer-associated membrane receptors or proteases rather than at more general biomarkers of the tumor environment, such as lowered extracellular pH. Further, many peptide delivery/uptake vehicles rely on endocytosis as the mechanism of internalization which is often limited by endosomal entrapment of the drug payload. Here, we present a strategy for the specific targeting and pH-triggered cytosolic delivery of the cancer chemotherapeutic doxorubicin (DOX) to HeLa cells using the pH Low Insertion Peptide (pHLIP). In work presented here, DOX was appended to pHLIP as either a single drug moiety or displayed as multiple copies (~4 per peptide) on the surface of a generation three dendrimer and release is driven by the reduction of disulfide bonds in the cytosol. The latter strategy was aimed at increasing the amount of DOX per pHLIP that could be delivered intracellularly. Biophysical analysis showed that both pHLIP-DOX conjugates inserted into membrane bilayers in a pH-dependent manner. Time-resolved confocal microscopy showed distinct differences between the conjugates in their intracellular release and nuclear localization of DOX. At 48 h post-delivery, pHLIP displaying a single disulfide-linked DOX showed significantly greater DOX in the nucleus than the dendrimer construct, suggesting a slower release rate. However, at 72 h nuclear accumulation was identical. Both constructs exhibited ~80% inhibition of cellular proliferation at 72 h post treatment at 10 μ M. Although, up to 17% greater anti-proliferative effects were observed with the dendrimeric complex at concentrations ranging from 0.16 μ M to 0.63 μ M. Our data demonstrate that dendrimeric display of DOX on the pHLIP carrier (1) allows for more DOX cargo per peptide, (2) does not

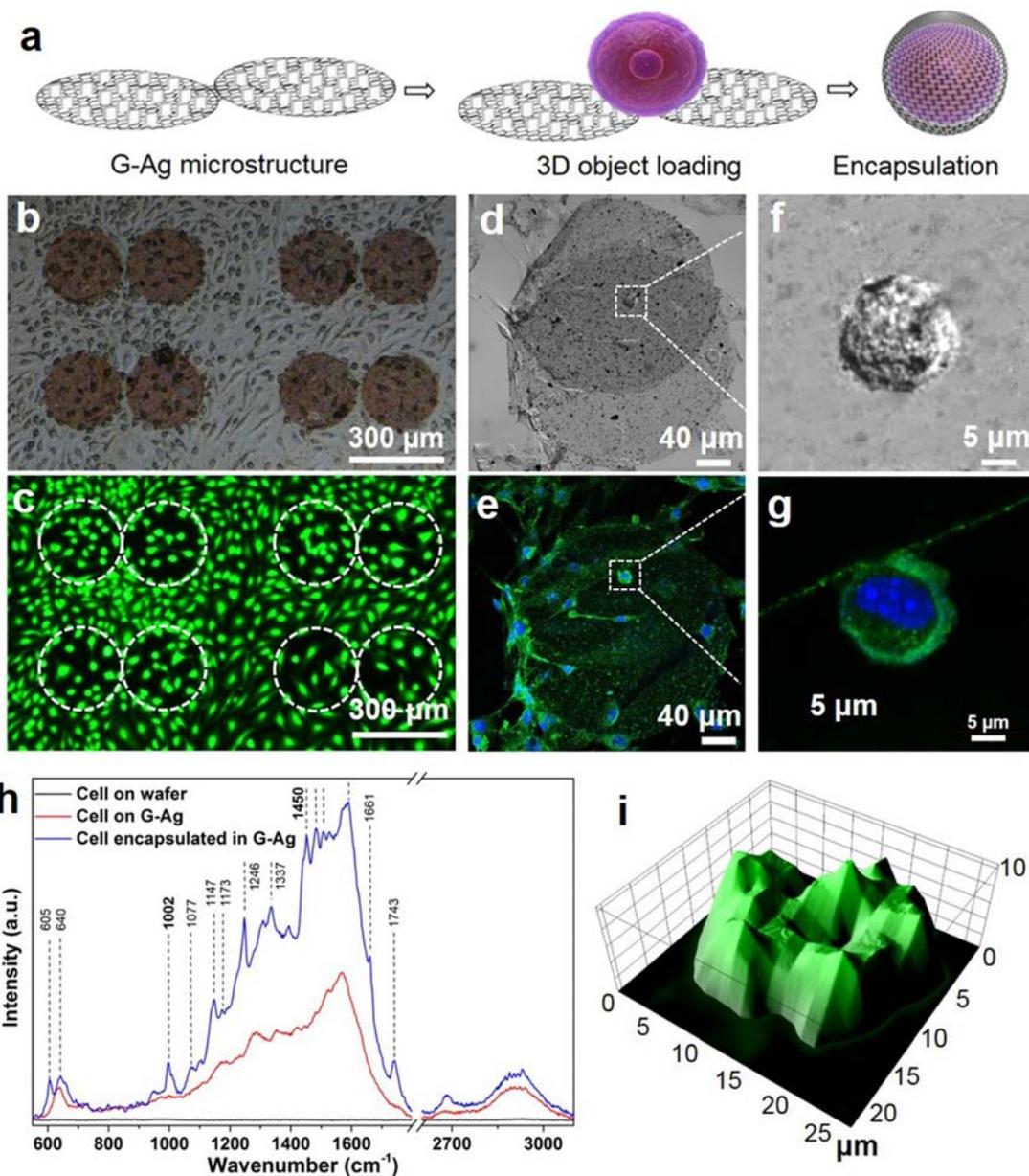
disrupt pHLIP's membrane-insertion behavior eliminating endosomal sequestration of DOX, and (3) facilitates temporally-controlled release that augments the cytotoxicity of DOX, particularly at low concentrations. Cumulatively, this study demonstrates the utility of the pHLIP-dendrimer conjugate system for the controlled delivery and modulation of drug efficacy through multivalent display and points to its use for multidrug delivery.

COLL 612

Flexible ultrathin graphene microstructures for 3D biosensing

Weinan Xu¹, weinanxu@gmail.com, Jayson Pagaduan¹, Qi Huang¹, David H. Gracias². (1) Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States (2) Johns Hopkins University, Baltimore, Maryland, United States

A major challenge in biosensing is that conventional biosensors are flat and rigid while cells and tissues are 3D and soft. Hence, there is an urgent need to develop electrical and optical biosensing platforms that are 3D and flexible so that they conform to the cell membrane. We discuss a flexible 3D biosensor composed of ultrathin graphene that has been coated with silver nanocubes (G-Ag). The graphene film was non-covalently functionalized with temperature responsive polymer brushes, so that the G-Ag microstructures can self-fold into well-defined 3D geometries. In addition, the self-folding G-Ag microstructures can encapsulate 3D objects such as microparticles and live cells with conformal contact to the surface of target. Strong Raman signals from the encapsulated live cell can be detected due to its close proximity to silver nanocubes, and 3D chemical information from the entire cell membrane can be obtained with high resolution. This new class of ultrathin 3D shell biosensors offers the possibility for 3D optical biosensing with high signal to noise ratios.



COLL 613

Ligand mediated exchange of oxidation state dependent ROS scavenging activity of cerium oxide nanoparticles

Vaishwik Patel¹, **Ajay Karakoti**^{1,2}, akarakoti@gmail.com. (1) Biological and Life Sciences, School of Arts and Sciences, Ahmedabad University, Ahmedadab, Gujarat, India (2) School of Engineering and Applied Science, Ahmedabad University, Ahmedabad, Gujarat, India

Cerium oxide nanoparticles (CNPs) are regarded as universal inorganic antioxidant that is capable of scavenging multiple reactive oxygen species (ROS) such as superoxide,

peroxide, nitric oxide etc. This nanozyme like activity of cerium oxide has been employed in realizing multiple applications such as treatment of tumours and cancers, radiation protection and development of sensors. The oxidation state of cerium in CNPs play an important role in determining which ROS species can be scavenged. It has been established that partially reduced CNPs with higher Ce^{3+}/Ce^{4+} ratio can scavenge superoxide and nitric oxide while stoichiometric CNPs with predominant Ce^{4+} can scavenge peroxide species. The redox potential for oxidation/reduction of surface cerium ions plays a major role in oxidation or reduction of ROS species. In this study we show that the fundamental redox potential of CNPs can be altered by modifying its surfaces with selected ligands. CNPs with different Ce^{3+}/Ce^{4+} ratios were synthesized by wet chemical synthesis and thermal hydrolysis method. As synthesized particles were functionalized with triethyl phosphate (TEP) and tris(2,4,6-trimethoxyphenyl) phosphine (TTMPP) ligands to modify its redox properties. Functionalized CNPs were characterized using light scattering, electron microscopy, UV-Vis, IR and fluorescence spectroscopy to ascertain the changes in the properties of bare nanoparticles post functionalization with ligands. It was found that the ROS scavenging properties of both reduced and stoichiometric CNPs are influenced by surface functionalization with ligands. Modification of stoichiometric CNPs with TEP increases its ability to scavenge superoxide species while leaving the properties of reduced ceria unaltered. On the other hand TTMPP imparts peroxide scavenging ability to reduced CNPs and does not alter the peroxide scavenging activity of stoichiometric ceria. Thus we conclude that the ROS scavenging of CNPs can be tuned independent of the oxidation state by changing their redox potential. TEP and TTMPP ligands with their differences in sigma donor and pi acceptor properties can differentially influence the redox properties of nanozymes (CNPs).

COLL 614

New method for quantifying low-energy electron emission from clinically relevant nanoparticles

Laura Cramer¹, lrcramer1@vt.edu, Benjamin P. Coughlin¹, Sijumon Kunjachan², Oliver Tillement³, Ross Berbeco², E Charles H. Sykes¹. (1) Chemistry, Tufts University, Somerville, Massachusetts, United States (2) Department of Radiation Oncology, Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts, United States (3) Institut Lumière Matière, Lyon-1 University, Lyon, France

Low energy electrons, defined as having energy in the 3-20 eV range, have been shown to induce DNA damage. This damage remains localized due to the short mean free path of low energy electrons (LEEs), around 1-10 nm in solution. It is thought that the therapeutic effects from radio sensitization nanoparticles (NPs) can be attributed to emission of these LEEs. An X-ray photoelectron spectroscopy (XPS) set-up has been used to study LEE emission from NP samples and quantify the number and energy of emitted electrons. These results will aid in the development of a universal tool to quantify and measure LEE emission from NPs. This will in turn provide valuable knowledge for the development of therapeutic NPs and a new method to understand

their mechanism of action. Our measurements were performed on small NPs composed of mostly polysiloxane, chelated with different metals (Gd, Bi, and Na) to study the effect of LEE emission as a function of the chelated metal. We have reproducibly measured the energy distribution and peak for these clinically relevant nanoparticles.

COLL 615

Targeted perfluorocarbon nanoparticles for disclosing critical information of lung cancer

Lina Wu^{1,2}, linawuhmu@hotmail.com, **Xiuan Xu**¹, **Jiaqi Ping**¹, **Yingbo Li**¹, **Kai Wang**^{1,2}, **Baozhong Shen**^{1,2}. (1) Molecular Imaging Research Center (MIRC), Harbin Medical University, Harbin, Heilongjiang, China (2) TOF-PET/CT/MR center, The Fourth Hospital of Harbin Medical University, Harbin, Heilongjiang, China, Harbin, China

Lung cancer is one of the leading cause of cancer deaths worldwide. The five-year survival rate for lung cancer (17.8 percent) is notably less than malignancies from the colon (65.4 percent), breast (90.5 percent) and prostate (99.6 percent). Finding new treatments is crucial. Fluorine-19 (¹⁹F) magnetic resonance (MR) molecular imaging has emerged as a unique non-invasive and quantitative imaging approach with wide research and clinical applications. Endogenous ¹⁹F is found primarily in bones and teeth as solid fluorides with undetectable magnetic resonance signals, therefore exhibiting a minimal background noise and potentially very strong signal-to background ratio in MR. Fast developed nanomedicine created promising opportunities for cancer detection. We synthesized Folate receptor (FR) targeted perfluorocarbon(PFC) nanoparticles(NPs) to *in vivo* disclose the relationship between the FR expression and tumor proliferation with MR molecular imaging. FR overexpresses in various epithelial cancers, and it holds great potential as an important diagnostic and prognostic biological marker. Intracellular nanoparticles uptake was measured by fluorescence microscopy and flow cytometry using H460 (FR-positive) and A549 (FR-negative) cell lines. ¹⁹F MR imaging of H460 (n=10) and A549 (n=10) subcutaneous tumor models was performed following intravenous injection of FR-targeted or non-targeted PFC NPs. The concentration of PFC in tumors at different time points were quantitatively compared. 3'-deoxy-3'-¹⁸F-fluorothymidine (¹⁸F-FLT) PET/CT imaging of H460 (n=4) and A549 (n=4) tumors, and Ki-67 immunohistochemistry staining were performed to evaluate the tumor proliferation and compared with the result from *in vivo* data of FR-targeted ¹⁹F MR molecular imaging. Here we find ¹⁹F MR imaging with FR-targeted PFC NPs can be used as a powerful diagnosis method in difference of FR-positive and FR-negative lung cancer. There is positive correlation between folate receptor expression and tumor proliferation. Moreover, the proliferation of lung cancer can be indirectly disclosed by ¹⁹F MR molecular imaging with FR-targeted NPs.

COLL 616

Development of a dexamethasone prodrug (ZSJ-0228) micelle formulation for effective and safe treatment of lupus nephritis

*Zhenshan Jia, Xiaobei Wang, Xin Wei, Gang Zhao, Kirk W. Foster, Fang Qiu, Yangyang Gao, Fang Yuan, Fang Yu, Geoffrey M. Thiele, Tatiana K. Bronich, James R. O'Dell, **Dong Wang**, dwang@unmc.edu. Univ Nebraska Medical Ctr, Omaha, Nebraska, United States*

Lupus nephritis (LN) is a major complication of systemic lupus erythematosus (SLE). While glucocorticoids (GC) are frequently being used as the first line treatment for LN, chronic exposure to GC has been associated with severe side effects, such as osteoporosis and immune suppression. To address this major clinical challenge, we have developed a polyethylene glycol (PEG)-based macromolecular dexamethasone prodrug (ZSJ-0228), which self-assembles into micelles. When compared to the dose equivalent daily dexamethasone phosphate sodium (Dex) treatment, monthly intravenous administration of ZSJ-0228 for 2 months significantly improved the survival of lupus-prone NZB/W F1 mice and was much more effective in normalizing proteinuria, with clear histological evidence of nephritis resolution. Different from the dose equivalent daily Dex treatment, monthly ZSJ-0228 administration has no impact on the serum anti-double stranded DNA (anti-dsDNA) antibody level but can significantly reduce renal immune complex deposition. No significant systemic toxicities of GC (e.g. total IgG reduction, adrenal gland atrophy and osteopenia, etc.) were found to associate with ZSJ-0228 treatment. In vivo imaging and flow cytometry studies reveal that the fluorescent-labeled ZSJ-0228 primarily distributes to the inflamed kidney after systemic administration, with renal myeloid cells and proximal tubular epithelial cells mainly responsible for its kidney retention. Collectively, these data suggest that the novel prodrug micelle design of ZSJ-0228 can greatly potentiate and prolong the local anti-inflammatory and immunosuppressive effects of Dex by passively targeting and retaining the prodrug to the inflamed kidneys via subcellular sequestration. Pending further optimization, it may be developed into an effective and safe therapy for improved clinical management of LN.

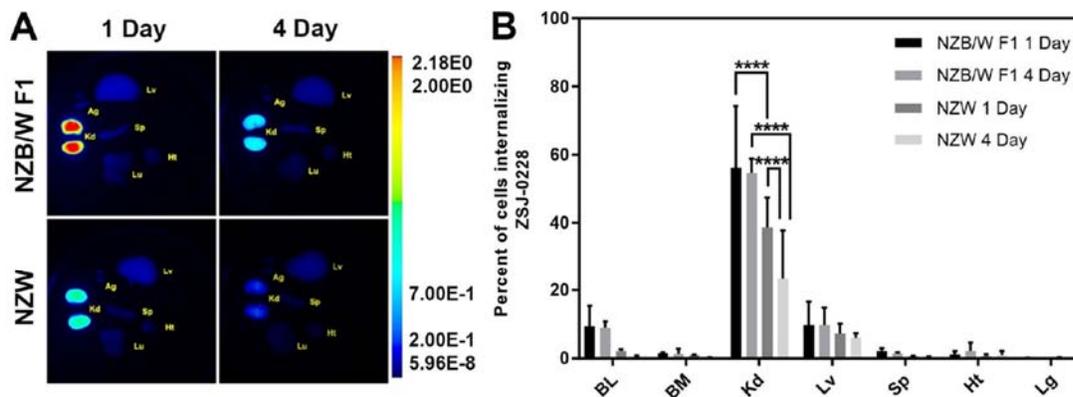


Figure 1. Passive targeting and retention of ZSJ-0228 at the kidneys of NZB/W F1 mice. **A.** Representative optical images of organs isolated from a NZB/W F1 mouse and a NZW mouse (healthy control). **B.** Flow cytometry analysis of cells isolated from organs of NZB/W F1 and NZW mice.

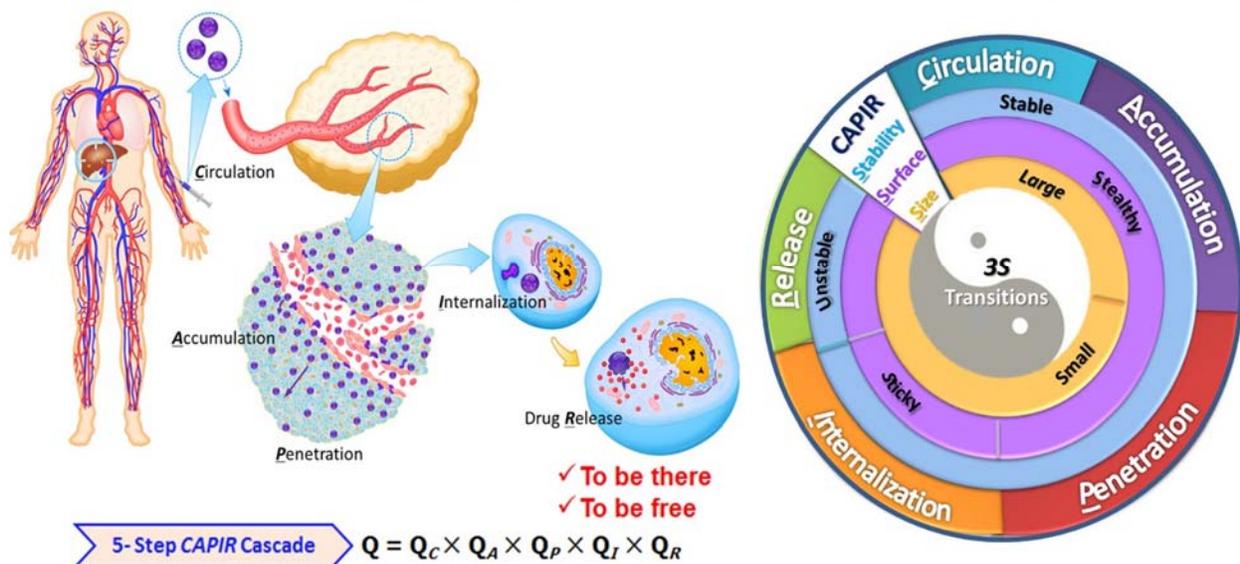
COLL 617

Polymeric nanomedicine: Nanoproperty synchronization

Youqing Shen, shenyq@zju.edu.cn, Zhuxian Zhou. Chem Biological Eng Dept, Zhejiang University, Hangzhou, China

The cancer drug delivery process is a cascade of five steps consisting of Circulation in blood, Accumulation and Penetration into the tumor, cellular Internalization and intracellular drug Release, or the CAPIR cascade. Thus, only if a nanomedicine efficiently goes through all the steps would it realize high therapeutic efficiency. The ability of a nanomedicine accomplishing the CAPIR steps is mainly determined by its three key nanoproperties, i.e., Size, Surface and Stability (3S nanoproperties), whose optima are different and even opposite in different steps. Thus, the utmost challenge in design of effective cancer nanomedicine is how to integrate and synchronize these incompatible 3S nanoproperties into one system. Here, we present a concept of a cluster bomb-like nanocarrier that synchronizes pegylation-to-depegylation, large-to-small size, and neutral-to-positive charge, stable-to-instable (i.e. 3S nanoproperty) transitions, essential for accomplishing the CAPIR cascade. Another example is the lipidic charge-reversal polyplexes for effective gene delivery.

Nanomedicine for Cancer Drug Delivery: The CAPIR Cascade and the 3S Nanoproperty Transitions



COLL 618

Biomimetic polymer-based self-assembled nanomedicine

Sebastien Lecommandoux, lecommandoux@enscbp.fr. LCPO-ENSCP, University of Bordeaux, Pessac, France

Polymers represent an important class of organic compounds that are used for many years in the development of biomaterials. Among them, amphiphilic block copolymers are among the most attractive systems for drug delivery applications. We report here an overview on the self-assembly in water of amphiphilic block copolymers into different nanomedicines, mainly focusing on polymer vesicles, also referred as polymersomes, and their applications in loading and controlled release of both hydrophilic and hydrophobic molecules and biomolecules.

We pay special attention to polysaccharide and polypeptide-based block copolymer vesicles and their development in nanomedicine. Indeed, the field of synthetic polypeptides has seen many significant advances in recent years, including studies on block and hybrid copolypeptides that form vesicles, fibrils, and other structures with potential applications in medicine and materials chemistry. However, the development of glycosylated polypeptides has not kept pace, primarily due to the inability to readily synthesize glycopolypeptides in a controlled manner. Glycosylation of natural proteins provides diverse functionality such as mediation of recognition events, modification of protein conformations, ect, that may find interest and application in biomedical field. In this context, we developed over the last years synthetic strategies for the design of glycosylated polypeptides and polysaccharide-polypeptide biohybrids with controlled placement of sugar functionality. We were especially interested in designing amphiphilic copolymers able to self-assemble into well-defined micelles and vesicles that can advantageously be loaded with drugs and present a surface with multivalent presentation of bioactive saccharides or oligosaccharides. The ability of these

nanoparticles for different biomedical applications, from drug-delivery to inhibitor, will be presented. We especially evidenced the particular benefit of nanoparticles and their multivalency toward the interaction with biological receptors.

COLL 619

Elevated levels of hydrogen peroxide in mesenchymal-like cancer cells can selectively trigger the dissolution of silver nanoparticles

Ravi Singh, rasingh@wakehealth.edu. *Cancer Biology, Wake Forest School of Medicine, Winston-Salem, North Carolina, United States*

Acquisition of a high-mesenchymal cell state by human tumors and cancer cell lines leads to increased cellular plasticity and may contribute to development of cancer drug resistance and tumor recurrence. Although cell plasticity is generally believed to be a protective mechanism for cancer cells, we have discovered that this may also be an exploitable vulnerability. We discovered that cancers that express high levels of ZEB1, a transcription factor that drives the dedifferentiation program known as epithelial-mesenchymal transition (EMT) and is associated with poor prognosis in many tumor types, also generate high levels of hydrogen peroxide (H_2O_2), which can be exploited as a trigger for release of cancer therapeutics. In the presence of oxidizing agents like H_2O_2 , silver nanoparticles (AgNPs) dissolve to release Ag^+ . Therefore, we investigated a controlled release mechanism whereby elevated baseline levels of H_2O_2 in ZEB1^{high} cells leads to dissolution of AgNPs to release Ag^+ , which then causes cell death. We quantified endogenous levels of H_2O_2 and sensitivity to AgNP exposure in a panel of ZEB1^{high} and ZEB1^{low} breast cancer cells and found that ZEB1^{high} cancer cells generated significantly more H_2O_2 and were 5-10 fold more sensitive to AgNPs than ZEB1^{low} cells. By transmission electron microscopy, we observed substantial degradation of AgNPs in endosomes of ZEB1^{high}, MDAMB231 cells but no degradation of AgNPs in ZEB1^{low} non-cancerous MCF-10A cells. AgNP exposure had no effect on cellular redox balance, endoplasmic reticulum stress, DNA damage, and mammary cell polarity in non-cancerous breast epithelial cells, but caused significant damage and apoptosis in ZEB1^{high} breast cancer cells. We found also that ovarian, lung, colorectal, and prostate cancer cell lines exhibiting the ZEB1^{high} mRNA profile were 5 to 500 fold more sensitive to AgNP exposure compared to cancers that came from the same tissue but had a ZEB1^{low} mRNA profile. Intravenous injection of AgNPs significantly reduced ZEB1^{high} MDA-MB-231 tumor growth in mice. No difference in weight between PBS and AgNP treated mice was observed, nor were overt signs of toxicity noticeable (i.e. hunched posture/immobility, and rapid or shallow breathing). Our discovery that ZEB1 is a biomarker that can predict which cancers are most likely to respond to AgNP therapy increases the possibility of future human clinical trials of AgNPs for treatment of well-selected patients.

COLL 620

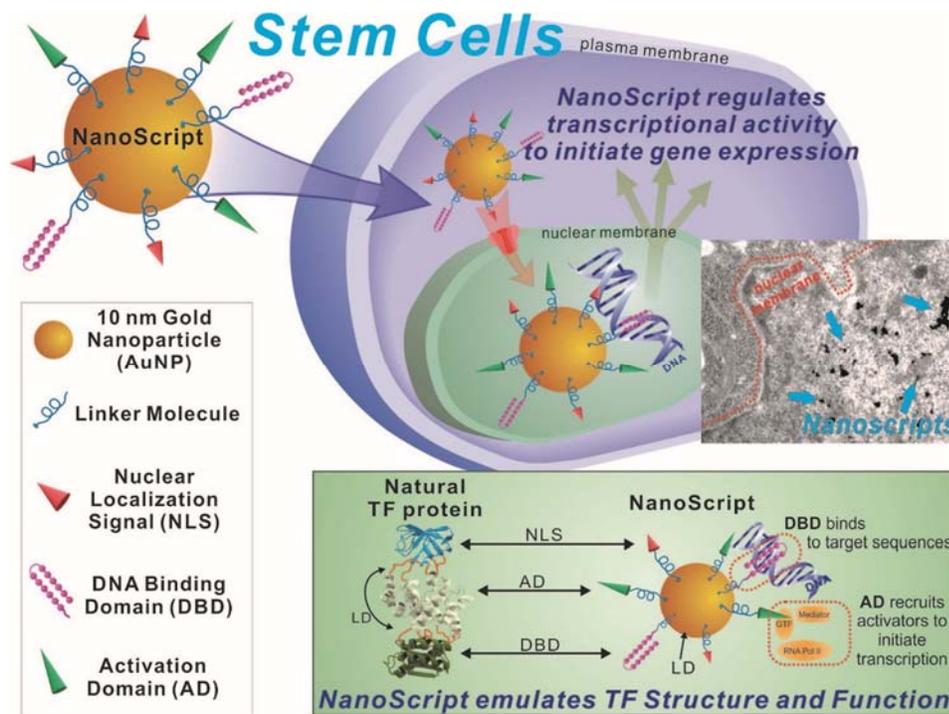
Bio-inspired nanoparticle-based transcription factor to control stem cell fate and function

***Ki-Bum Lee**, kbnano@gmail.com. Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey, United States*

This presentation will focus on the interface between nanoscience and stem cell biology. Even though it is well-established that stem cell fate is regulated by interactions that occur between microenvironmental cues and intrinsic cellular programs, our understanding of the function of the microenvironment and gene expression in stem cells is hampered by the limitations of conventional methods and the lack of extensive knowledge of multiple regulatory signals.

To this end, the long-term goal of our research program is to develop a bio-inspired platform that can replicate the structure and function on endogenous proteins called transcription factor (TF) proteins, which are responsible for orchestrating overall stem differentiation into specific cell lineages. Our bio-inspired platform called **NanoScript**, is a nanoparticle-based transcription factor that behaves and function just like natural TF proteins. This NanoScript platform is designed to be gene-specific and can effectively activate targeted gene in a non-toxic and non-viral manner [**Figure 1.**]. Potentially, this study will not only open the gateway of a more promising approach to treating patients suffering from human patient-derived stem cells, but also establish NanoScript as a new platform to investigate targeted epigenetic modulation that can be useful for effective stem cell differentiations, stem cell-based cell replacement therapies, and cellular reprogramming.

In this presentation, a summary of the most updated results from these efforts and future directions will be discussed.



COLL 621

Formulation of dual component solid drug nanoparticles for improved oral bioavailability of Darunavir and Ritonavir

Alison C. Savage¹, asavage1@hotmail.co.uk, **Samantha J. Ashcroft**¹, **Helen Box**², **Joanne Sharp**², **Megan Neary**², **Andrew Owen**², **Steve Rannard**¹. (1) Chemistry, University of Liverpool, Hereford, United Kingdom (2) Molecular and Clinical Pharmacology, University of Liverpool, Liverpool, United Kingdom

Many active pharmaceutical ingredients (API) exhibit poor aqueous solubility, which can often impact on the bioavailability of the drug when taken as a therapy. Recently, a strategy for formulating antiretroviral drugs into solid drug nanoparticles (SDNs) has been presented, with the resulting products exhibiting enhanced oral pharmacokinetics (PK). Preparation of these nanoparticles relies on an emulsion-templated freeze-drying method to screen different CDER listed polymers and surfactants, with the drug dissolved in an organic phase and water soluble polymers and surfactants present in the aqueous phase. Once ideal excipients are identified and studied for reproducibility, stability and pharmacological behaviour, the method can be translated to spray-drying for scale-up and manufacture. Antiretroviral drugs are often taken in combinations as part of a HIV drug regimen which act on multiple viral targets. This is known as highly active antiretroviral therapy (HAART) and often involves antiretroviral drugs being administered with ritonavir, known to boost the half-life of certain antiretrovirals. We have adopted the solid drug nanoparticle strategy with the anti-retroviral drugs Darunavir (DRV) and Ritonavir (RTV) to prepare dual component SDNs to combine two APIs into one nanoparticle-containing powder feedstock. *In vitro* pharmacological

testing isolated the three best performing formulations by determining the apparent permeability of the SDNs across Caco-2 and triple culture monolayers, whilst *in vivo* studies established the steady state pharmacokinetic profile of the best performing SDN. Steady-state multiple-dosing studies determined, using an initial loading dose followed by a 50 % lower maintenance dose, that there is potential for a considerable dose reduction without compromising PK exposure. This data provides preclinical demonstration of the world's first DRV/RTV fixed-dose-combination formulation with a potential for dose reduction of both DRV and RTV whilst maintaining drug concentrations in the therapeutic window. The scale-up manufacture of the best SDN candidate by spray-drying has provided the manufacturing scale necessary to potentially pursue first in human clinical evaluation.

COLL 622

Structural DNA nanotechnology: Complex self-assembly and biomedical applications

Yonggang Ke, yonggang.ke@emory.edu. Biomedical Engineering, Emory University, Atlanta, Georgia, United States

A key challenge in nanotechnology is to design and fabricate nanostructures and nanodevices. Such systems can serve as platforms for basic science research (structural biology, molecular biology, for instance) at nanoscale, and for practical applications. Bottom-up structural DNA nanotechnology has attracted significant attentions due to its programmability and its precise control of matter at nanoscale. This seminar will open with a brief introduction of structural DNA nanotechnology, followed by discussing our recent progress in making massive/complex DNA nanostructures and dynamic DNA devices. Particularly, I will discuss how we can construct fully addressable GDa nanostructures from modular DNA components called "DNA bricks", and dynamic DNA structure transformation. DNA nanostructures has also shown increasing capabilities for basic science research, and for practical applications, such as fabrication of single-molecule functional nanoscale materials. I will present our most recent works related to potential drug nanodelivery systems engineered by using DNA self-assembly.

COLL 623

Dynamic topographical structure: A new parameter for designing nanomedicine

Hao Cheng, hcheng@coe.drexel.edu, Hao Zhou, Zhiyuan Fan, Peter Y. Li. Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States

Nanomaterials have broad biomedical applications. Although their physicochemical properties such as shape, size, elasticity and surface chemical composition are known to be pivotal in the design of nanomedicines. The impact of dynamic topographical

structure of nanomaterials has not attracted significant attention. In this talk, I will show the importance of this new parameter for nanomedicine design. We have found that nanomaterials blood circulation time could be dramatically extended by controlling the dynamic topographical structure of polyethylene glycol (PEG) shell on nanoparticles. Regular high density PEG shell does not have this effect. Previous studies of long circulating nanomaterials all focused on reducing nanoparticle uptake by macrophages. Surprisingly, our studies reveal that the dynamic effect extends nanoparticle blood circulation through a new mechanism, which does not involve macrophages. One of the major challenges of nanomedicines in cancer therapy is the inefficient diffusion of drug nanocarriers in solid tumors due to the high density of extracellular matrix in tumors. One old strategy is to conjugate matrix degrading enzymes on nanoparticle surfaces as the enzymes remove barriers for nanoparticle diffusion. However, successful animal studies have not been demonstrated. One reason is the conjugation of bioactive molecules on nanoparticle surfaces often reduces their blood circulation. We show that the problem can be circumvented by embedding matrix degrading enzymes in the PEG shell with dynamic structure instead of presenting the enzymes on the outmost surface of nanoparticles. The effects of prolonged nanoparticle blood circulation and enhanced diffusion in solid tumors dramatically enhanced nanoparticle accumulation and penetration in tumors, leading to a highly efficient antitumor efficacy. Thus, our platform technology of controlling topographical structure of nanocarriers may be valuable to enhance the clinical efficacy of a broad range of drug nanocarriers.

COLL 624

Structurally modulated codelivery of siRNA and Argonaute 2 for enhanced RNA interference

Jiahe Li¹, jiaheli@mit.edu, Connie Wu¹, Wade Wang¹, Yanpu He², Paula T. Hammond³. (1) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Chemical Engineering, MIT, Cambridge, Massachusetts, United States (3) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Small interfering RNA (siRNA) represents a promising class of inhibitors in both fundamental research and the clinic. Numerous delivery vehicles have been developed to facilitate siRNA delivery. Nevertheless, achieving highly potent RNA interference (RNAi) toward clinical translation requires efficient formation of RNA-induced silencing complex (RISC) in the cytoplasm. Here we coencapsulate siRNA and the central RNAi effector protein Argonaute 2 (Ago2) via different delivery carriers as a platform to augment RNAi. The physical clustering between siRNA and Ago2 is found to be indispensable for enhanced RNAi. Moreover, by utilizing polyamines bearing the same backbone but distinct cationic side-group arrangements of ethylene diamine repeats as the delivery vehicles, we find that the molecular structure of these polyamines modulates the degree of siRNA/Ago2-mediated improvement of RNAi. We apply this strategy to silence the oncogene STAT3 and significantly prolong survival in mice

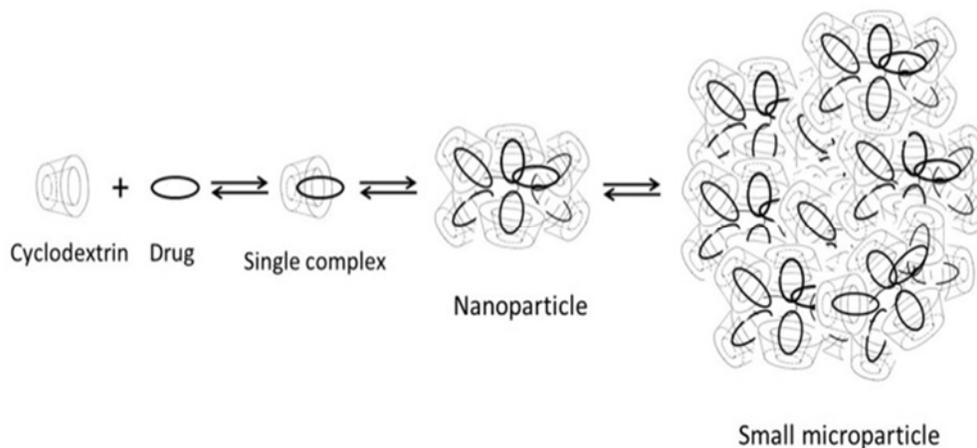
challenged with melanoma. Our findings suggest a paradigm for RNAi via the synergistic coassembly of RNA with helper proteins.

COLL 625

Physicochemical properties of self-assembled cyclodextrin nanoparticles and their application in drug delivery

Thorsteinn Loftsson, *thorstlo@hi.is. Faculty of Pharm. Sci., University of Iceland, Reykjavik, Iceland*

Drug/cyclodextrin complexes self-assemble in aqueous solutions to form nanoparticles or aggregates. The invisible complex aggregates with diameter of less than 250 nm are responsible for many of the physicochemical and biological properties of cyclodextrin complexes. Due to the aggregate formation aqueous drug/cyclodextrin solutions can behave more like dispersed nanoscale systems, such as nano-suspensions and liposomes, rather than true solutions. The drug/cyclodextrin nanoparticles are unstable and dissociate upon media dilution, heating or addition of organic solvent to the aqueous complexation media, a behavior that resembles that of micellar aggregates (i.e. micelles). Although the nanoparticles are unstable their stability can be increased by, for example, including water-soluble polymers in the aqueous complexation media. The drug/cyclodextrin complex nanoparticles can result in enhanced cyclodextrin solubilization of poorly soluble lipophilic drugs; they can serve as building blocks for ternary or higher order complexes; and they can be developed into nanoparticle drug carriers for targeted drug delivery. Several examples will be given of (1) how the aggregation affects analysis of cyclodextrin complexes, (2) how the aggregates affect cyclodextrin solubilization of drugs, (3) excipient-aggregate interactions, and (4) how the larger aggregates enhance topical drug delivery to the eye.



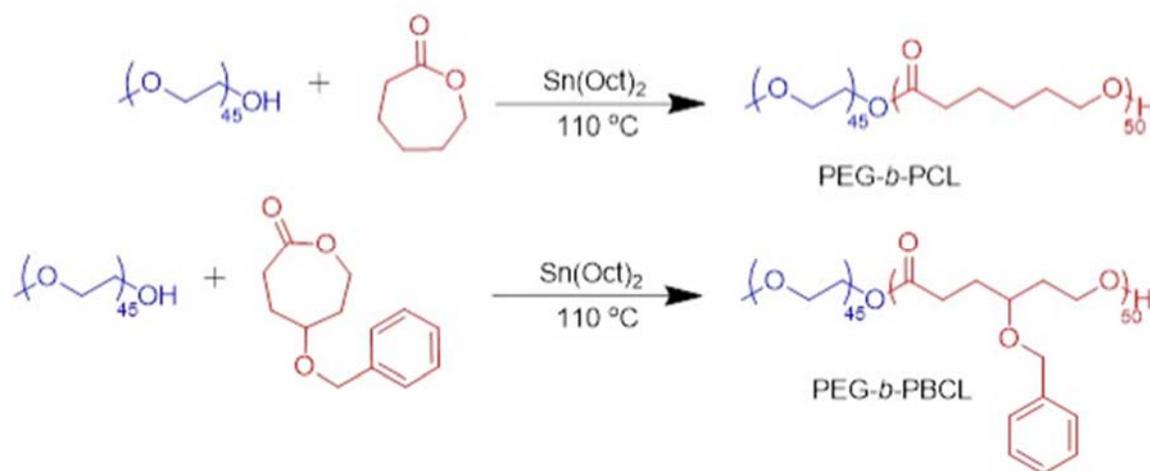
Self-assembly of drug/cyclodextrin complexes to form nanoparticles and small microparticles. The process is reversible that facilitates their elimination from biological systems.

COLL 626

Combination loading of doxorubicin and resveratrol in polycaprolactone polymeric micelles

Mihaela C. Stefan¹, *mci071000@utdallas.edu*, Katherine Washington¹, Ruvanthy Kularatne^{2,1}, Pooneh Soltantabar¹, Erika J. Calubaquib¹, Michael C. Biewer³. (1) Dept Chem UT Dallas, Richardson, Texas, United States (2) The University of Texas at Dallas, Richardson, Texas, United States (3) Dept of Chemistry, University of Texas at Dallas, Richardson, Texas, United States

Combined loading of doxorubicin (DOX) and polyphenol resveratrol (RSV) in amphiphilic polycaprolactone polymeric micelles generated an increased loading of DOX. Poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) (PEG-*b*-PCL) and poly(ethylene glycol)-*b*-poly(γ -benzyl- ϵ -caprolactone) (PEG-*b*-PBCL) (Scheme 1) were used to generate polymeric micelles which were employed to co-load DOX and RES. The increased loading was attributed to the favorable interactions of DOX and RSV and to the interaction with benzyl substituents of PEG-*b*-PBCL diblock copolymer micelles. Combination loaded micelles of PEG-*b*-PBCL diblock copolymer showed a significant improvement in DOX loading as compared to DOX only loaded PEG-*b*-PBCL. The encapsulation efficiency of DOX increased from 31.0% to 87.7% upon co-loading with RES. Combination loaded micelles also showed increased cytotoxicity to HeLa cells as compared to DOX only loaded micelles.



COLL 627

Self-assembled block copolymer micelles with tuned hydrolytic stability as efficient docetaxel delivery systems for breast cancer therapy

Uttam Satyal¹, *tue90799@temple.edu*, Vishnu D. Sharma¹, Harvey Hensley², Marc A. Ilies¹. (1) Department of Pharmaceutical Sciences, Temple University School of

Pharmacy, Philadelphia, Pennsylvania, United States (2) Temple Fox Chase Cancer Center, Philadelphia, Pennsylvania, United States

The purpose of this study was to assess and compare the in vivo stability, shelf stability, cargo protection and to control of drug loading and drug release profiles of polymeric drug delivery systems (DDSs) based on interfacially-engineered PEG-PCL block copolymers. These novel polymeric micelle DDSs were expected to safely transport the toxic chemotherapeutic drug docetaxel and selectively deliver it to the tumor site with an elevated percent of the injected dose reaching the solid tumors and eliciting enhanced tumor killing in an orthotopic model of triple negative breast cancer in female SCID mice. We will present experimental results confirming the efficiency of the novel polymeric micelles, together with structure-property relationships. Specifically, docetaxel was loaded in micelles using co-nanoprecipitation method. Encapsulation efficiency was evaluated using LC-MS while in vitro drug release profile was obtained in sink conditions and was evaluated via HPLC. The stability of the self-assembled nanosystems in blood serum, and in the tumor environment was determined via NMR, GPC, fluorescence spectroscopy and via DLS. Results to be presented confirmed that the engineered interface of the triblock copolymers allows simplification and better control of the DDS formulation and drug loading process, higher drug loading capacity, superior enzymatic stability en-route to tumor and a controlled, focused release of docetaxel into the tumors, translating into an efficient tumor growth control doubled by an excellent toxicity profile, as proved by in vivo results in experimental animals.

COLL 628

How to increase micelle loading by manipulating the preparation approach for frozen block copolymer micelles? A theoretical view

Ramanathan Nagarajan, ramanathan.nagarajan.civ@mail.mil. Natick Soldier RDEC, Natick, Massachusetts, United States

Increasing drug or nutrient loading in nanocarriers is of interest to developing new drug or nutrient delivery technologies. It is of interest to develop approaches that can maximize the loading capacity of block copolymer micelles, which are important nanocarrier systems. Experiments show that when the hydrocarbon molecule is a good solvent for the hydrophobic block of the copolymer, one can achieve high equilibrium solubilization capacities of the order of 1 to 3 g of the hydrophobic molecule per g of the hydrophobic block of the copolymer. However, despite their hydrophobicity, rarely drug molecules constitute good solvents for the polymer blocks. Therefore, a generic method that could maximize the micelle loading is desirable, independent of the specificity of the drug or nutrient molecule. We explore through thermodynamic modeling whether the loading capacity of micelles can be increased by manipulating how micelles containing solubilize are prepared. It is widely recognized that a vast number of micelles generated in water from amphiphilic block copolymers are non-equilibrium structures because of the strong hydrophobicity of the hydrophobic block of the copolymer. Typically, the micelles are prepared by a kinetic process, first allowing molecular scale

dissolution of the block copolymer in a common solvent that likes both the blocks and then gradually replacing the common solvent by water to promote the hydrophobic blocks to aggregate and create the micelles. By incorporating the solubilize during the micelle preparation process we may be able to “freeze” the micelles at conditions where the solubilize loading is high. The properties of the solubilize, the choice of the common solvent and their interactions with the hydrophobic block of the copolymer all control the eventual micelle size and loading capacity. The theoretical model predicts this micelle loading capacity as a function of the molecular parameters that control the formation of solubilize carrying frozen micelles.

COLL 629

Stabilizing colloidal drug aggregates for drug-rich nanoparticle formulations

Ahil Ganesh¹, ganesh.ahil@gmail.com, Jennifer Logie¹, Christopher McLaughlin¹, Brian Shoichet², Molly S. Shoichet¹. (1) University of Toronto, Toronto, Ontario, Canada (2) Univ of Calif San Fran, San Francisco, California, United States

The aggregation of hydrophobic small molecules into colloidal particles is a major contributor towards false hits during the drug development process. Their formation is governed by a critical aggregation concentration, below which the compound exists as soluble monomers. Adsorption of proteins to the colloid surface leads to non-specific enzyme inhibition and false-positives in high-throughput drug screening. Additionally, the inability of colloidal aggregates to diffuse across cell membranes results in an apparent loss of cytotoxic activity for a number of chemotherapeutics, leading to false-negative results in cell-based assays. While colloids are viewed as nuisance artefacts, their drug-rich composition makes them attractive as intentional formulations; however, the transient stability of colloidal aggregates limits their use. Herein, we investigated the use of polymeric excipients and protein coronas to stabilize colloidal aggregates of chemotherapeutics for applications in drug delivery.

Two strategies were employed to formulate stable colloidal drug aggregates of chemotherapeutics: 1) co-formulation with polymeric excipients such as polysorbate 80 or a custom-synthesized poly(D,L-lactide-co-2-methyl-2-carboxytrimethylene carbonate)-graft-poly(ethylene glycol), or 2) passivation of the colloidal surface to form a protein corona comprising albumin or trastuzumab. Co-formulation of colloidal aggregates with either polymeric excipients or protein coronas greatly improved their stability; both strategies yielded colloids stable over 48 h in buffered saline and serum-containing media. Polymeric excipients significantly reduced protein adsorption to colloids and decreased enzyme inhibition classically observed with colloidal aggregates. Protein coronas composed of the anti-HER2 antibody, trastuzumab, were able to induce selective uptake by target HER2-overexpressing cells where coronas comprising a non-targeted IgG did not lead to internalization.

With these stabilized and targeted colloidal formulations, further investigation into the biological fate of colloidal drug aggregates is possible. These strategies may allow us to

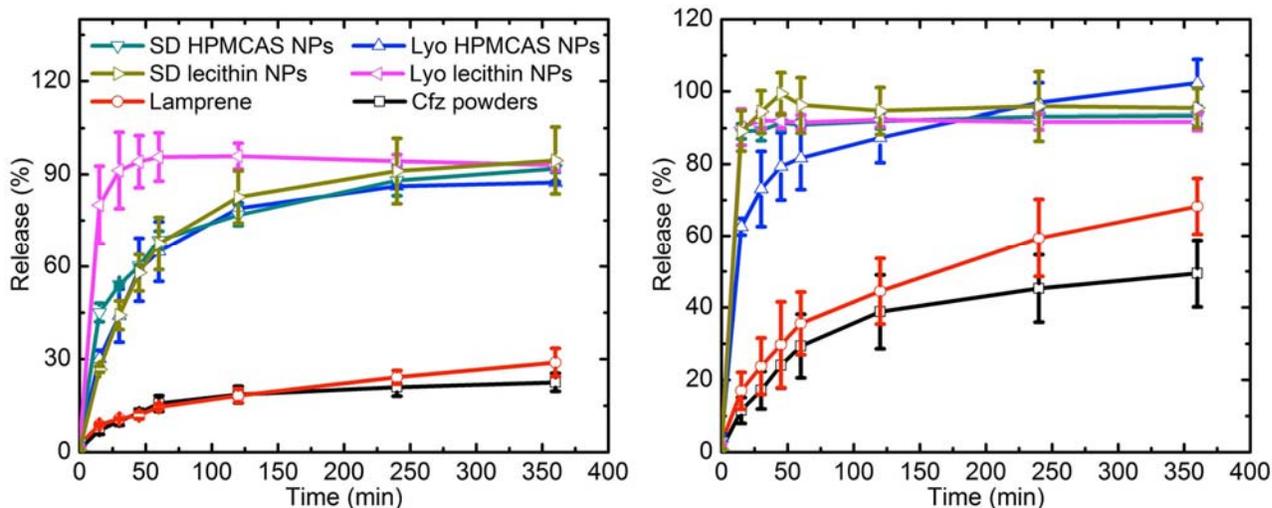
repurpose what has long been thought of as a nuisance artefact in drug screening into a useful formulation strategy.

COLL 630

Rapid recovery of clofazimine nanoparticles with long-term storage stability as anti-cryptosporidium therapy

Jie Feng¹, jiefeng@princeton.edu, Yingyue Zhang¹, Simon McManus¹, Kurt Ristroph¹, Hoang Lu¹, Kai Gong², Claire White², Robert K. Prudhomme¹. (1) Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States (2) Civil and Environmental Engineering, Princeton University, Princeton, New Jersey, United States

While the formulation of nanoparticle suspensions has been widely applied in materials and life science, the recovery of nanoparticles from such a suspension into a solid state while preserving the original nanoscale properties remains a formidable challenge in the pharmaceutical and biomedical application of nanoparticles. Herein we combined Flash NanoPrecipitation (FNP) and spray-drying for nanoparticle formulation and recovery without compromising the dissolution kinetics of the active ingredient. Clofazimine was chosen to be the model drug, which has been recently repurposed as a potential treatment for cryptosporidiosis for global health. Clofazimine was encapsulated into nanoparticles with low-cost surface coatings, hypromellose acetate succinate (HPMCAS) and lecithin, which was required by the ultimate application to global health. Spray drying and lyophilization were utilized to produce dried powders with good long-term storage stability for application in hot and humid climatic zones. The *in vitro* release kinetics of spray-dried nanoparticle powders were compared to the analogous dissolution profiles from standard lyophilized nanoparticle sample, crystalline clofazimine powder and the commercially-available formulation. The spray-dried powders showed a supersaturation level up to 60 times equilibrium solubility and remarkably improved dissolution rates, similar to the lyophilized samples. In addition, the spray-dried powders with both surface coatings showed excellent stability during aging studies with elevated temperature and humidity. Considering oral delivery for pediatric administration, the spray-dried powders cause less mouth discoloration than crystalline clofazimine, and may be made into mini-tablets manufacture without any additional excipients. These results highlight the potential of combining FNP and spray-drying as a feasible and versatile platform to design and rapidly recover amorphous nanoparticles in a solid dosage form, with the advantages of satisfactory long-term storage stability, low cost, and easy scalability.



Dissolution kinetics of HPMCAS/lecithin NPs with different drying processes compared to clofazimine powder and Lamprene in (left) FaSSIF and (right) FeSSIF.

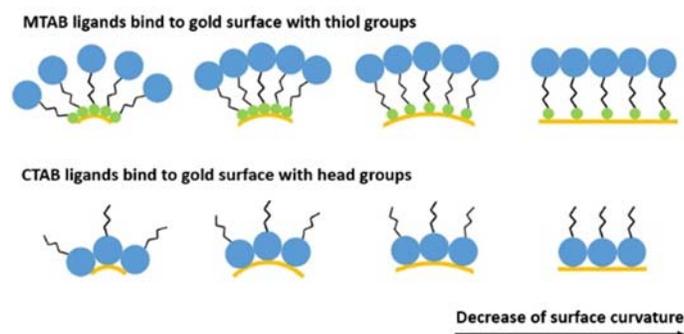
COLL 631

NMR analysis of ligand environments on gold nanoparticles: The effect of surface curvature and ligand binding modes

Meng Wu¹, mengwu4@illinois.edu, **Catherine J. Murphy**². (1) Chemistry, University of Illinois Urbana-Champaign, Urbana, Illinois, United States (2) Box 59-6, Univ of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Synthetic inorganic nanoparticles are often stabilized by an organic ligand shell that defines much of their chemical and biological properties, but little is known about the morphology and dynamics of these ligands. Here, we report an NMR-based analysis of (16-mercaptohexadecyl)trimethylammonium bromide (MTAB) functionalized gold nanospheres (AuNSs) with sizes from 1.5 nm to 40 nm and gold nanorods (AuNRs) with aspect ratios from 1.3 to 3.8. Broadened and shifted peaks in ¹H NMR spectra suggest MTAB ligands are bound to the nanoparticles. Aging experiments show that MTAB ligands desorb over time as MTAB-disulfide. The dissociation equilibrium is achieved over 20 days with less than 1% of the ligands staying free in the solution. Quantitative NMR shows that the ligand density of MTAB-AuNSs is size-dependent, ranging from 2.5 to 6 molecules per nm². The chemical shift analysis of the proton signals from the solvent-exposed head groups suggests an increasing degree of hydrocarbon chain packing until the sizes of the nanoparticles increase to 12 nm. The ligand environment of MTAB-AuNSs larger than 12 nm resembles to that of a planar surface. The anisotropic functionality of cetyltrimethylammonium bromide (CTAB) capped AuNRs at the ends and sides have been observed experimentally in other reports. However, T₂ relaxation curves for MTAB-AuNRs of different aspect ratios all decay mono-exponentially, similar to that of MTAB-AuNSs. The ligand density of MTAB-AuNRs is 2.5 molecules per nm², which is independent of the aspect ratios and similar to that of

MTAB-AuNSs with sizes larger than 12 nm. These results suggest that no differences in MTAB ligands on the sides and ends of the AuNRs have been observed, and that the MTAB ligands on the ends and sides both resembles those on a planar surface. The loss in ligand anisotropy in MTAB-AuNRs can be explained by the differences in ligand binding modes: CTAB binds to the gold surface by the bigger head groups whereas MTAB binds by the smaller thiol groups.



MTAB and CTAB ligand environments with decreasing surface curvature (for CTAB bilayers, only the inner leaflet is shown).

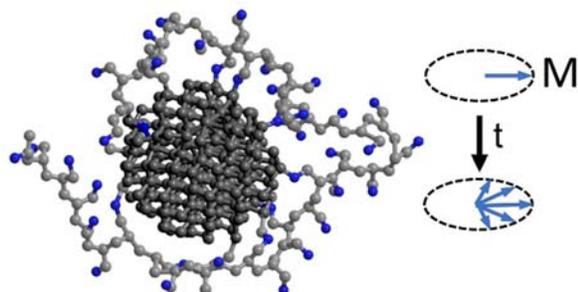
COLL 632

Dynamics and morphology of polymer-modified nanoparticle elucidated by NMR spectroscopy

Yongqian Zhang¹, **Charles G. Fry**¹, fry@chem.wisc.edu, Joel A. Pedersen², Robert J. Hamers². (1) Chemistry, University of Wisconsin- Madison, Madison, Wisconsin, United States (2) Univ of Wisconsin, Madison, Wisconsin, United States

Nanoparticles are frequently modified with polymer layers to control their physical and chemical properties, but little is understood about the morphology and dynamics of these polymer layers. We report here an NMR-based investigation of a model polymer-modified nanoparticle using multiple NMR techniques including ¹H NMR, DOSY, TOCSY, and T₂ relaxometry to characterize the dynamics of the nanoparticle-polymer interface. Using 5 nm detonation nanodiamond covalently linked to poly(allylamine) hydrochloride as a model system, we demonstrate the use of NMR to distinguish between free and bound polymer and to characterize the degree to which the segments of the nanoparticle-wrapping polymer are mobile (loops and tails) vs. immobile (trains). Our results show that the polymer-wrapped contain a large fraction of highly mobile polymer segments, implying that the polymer extends well into solution away from the nanoparticle surface. Flexible, distal polymer segments are likely to be more accessible to extended objects such as cell membranes, compared with polymer segments that are in close proximity to the nanoparticle surface. Thus, these flexible segments may be particularly important in

controlling subsequent interactions of the nanoparticles. While reported here for a model system, the methodology used demonstrates how NMR methods can provide important insights into the structure and dynamics at nanoparticle-polymer interfaces, leading to new perspectives on the behavior and interactions of polymer-functionalized nanoparticles in aqueous systems.



COLL 633

Optical evaluation of gold nanostars on polymer mats for uranyl detection

Hoa T. Phan¹, hoa-phan@uiowa.edu, **Amanda J. Haes**². (1) Department of Chemistry, University of Iowa, Iowa city, Iowa, United States (2) Chemistry, University of Iowa, Iowa City, Iowa, United States

Electrospun mats composed of amidoximated polyacrylonitrile for molecular isolation coupled with gold nanostar deposition for enhancement in surface-enhanced Raman scattering (SERS) is a powerful platform for the detection of uranyl from complex sample matrices. Herein, impacts of gold nanostar deposition on the SERS detection of uranyl are evaluated as a function of deposition method and spatial uniformity. Nanostar distribution on the mats is evaluated using localized surface plasmon resonance (LSPR) spectroscopy and bright field image color analysis while uranyl uptake is evaluated using SERS. Non-linear effects are noted spatially and related to local plasmonic properties of the nanostars, mat morphology, and uranyl concentration. Under optimal conditions, SERS signals of uranyl is dependent solely on uranyl uptake thus promoting the quantitative detection of uranyl on the polymer mats using gold nanostars. All in all, these findings are expected to serve as a quick, reliable, and reproducible platform for the detection of uranyl in the lab and field.

COLL 634

Light-enabled reversible self-assembly and tunable optical properties of stable hairy nanoparticles

Yihuang Chen¹, yihuang.chen@mse.gatech.edu, **Zhiqun Lin**². (1) Georgia Institute of Technology, Atlanta, Georgia, United States (2) School of Material Sci Engr, Georgia Institute of Technology, Atlanta, Georgia, United States

The ability to dynamically organize functional nanoparticles (NPs) via the use of environmental triggers (temperature, pH, light, or solvent polarity) opens up important perspectives for rapid and convenient construction of a rich variety of complex assemblies and materials with new structures and functionalities. Here, we report an unconventional strategy for crafting stable hairy NPs with light-enabled reversible and reliable self-assembly and tunable optical properties. Central to our strategy is to judiciously design amphiphilic star-like diblock copolymers comprising inner hydrophilic blocks and outer hydrophobic photoresponsive blocks as nanoreactors to direct the synthesis of monodisperse plasmonic NPs intimately and permanently capped with photoresponsive polymers. The size and shape of hairy NPs can be precisely tailored by modulating the length of inner hydrophilic block of star-like diblock copolymers. The perpetual anchoring of photoresponsive polymers on the NP surface renders the attractive feature of self-assembly and disassembly of NPs on demand using light of different wavelengths, as revealed by tunable surface plasmon resonance absorption of NPs and the reversible transformation of NPs between their dispersed and aggregated states. The dye encapsulation/release studies manifested that such photoresponsive NPs may be exploited as smart guest molecule nanocarriers. By extension, the star-like block copolymer strategy enables the crafting of a family of stable stimuli-responsive NPs (e.g., temperature- or pH-sensitive polymer-capped magnetic, ferroelectric, upconversion, or semiconducting NPs) and their assemblies for fundamental research in self-assembly and crystallization kinetics of NPs as well as potential applications in optics, optoelectronics, magnetic technologies, sensory materials and devices, catalysis, nanotechnology, and biotechnology.

COLL 635

Synthesis of bifunctional NHC-CO₂ adducts for SERS-based sensing on gold

Joseph F. DeJesus¹, jdejesus@vols.utk.edu, Michael J. Trujillo², Jon P. Camden², David M. Jenkins¹. (1) Chemistry, University of Tennessee, Knoxville, Knoxville, Tennessee, United States (2) Chemistry, University of Notre Dame, Notre Dame, Indiana, United States

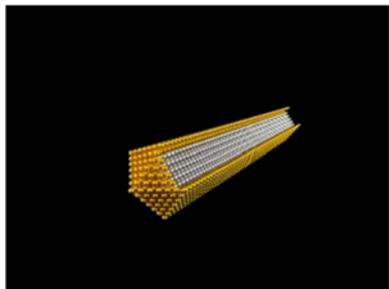
For surface enhanced Raman spectroscopy (SERS), thiol containing molecules commonly form the self-assembled monolayers (SAMs) that facilitate sensing. However, thiols have significant drawbacks that limit their viability in sensors such as low stability in oxidative conditions or extreme pHs. Recently, N-heterocyclic carbene (NHC) SAMs have been shown to circumvent a number of problematic issues that are known for thiol based SAMs. Key limitations for the development of functionalized NHC SAMs for SERS is a lack of straightforward SAM preparation as well as understanding functional group tolerances for bifunctional NHCs that are necessary for sensing. We present the first example of NHCs as a ligand platform for SERS. The design, synthesis and characterization of bifunctional NHC-CO₂ adducts, which can functionalize surfaces in solvent-free conditions, are described. The stability of the NHC ligands and post-synthetic functionalization are also studied in detail using SERS.

COLL 636

Epitaxial, ultra-thin Au coating as a barrier for oxidation damages for silver nanowires

Yangzhi Zhu, *yzhu026@ucr.edu*. University of California, Riverside, Riverside, California, United States

Silver nanowires (AgNWs) hold promise for applications such as transparent and flexible displays, solar cells, chemical/biological sensors, photonic circuits and scanning tunneling microscopies, but their susceptibility to damage from oxidation has limited their commercialization. Herein, we develop a room-temperature chemical coating technique to deposit an ultra-thin, epitaxial layer of Au on the AgNWs surface, which shields the AgNWs from oxidation, and thus it could represent a key to realize their commercial potential. Our work has shown that the Ag@Au core-shell nanowires are stable in air for at least 183 days (>6 months) and in physiological buffer solution (PBS) for at least 21 days. The thin Au coating did not introduce significant Au fluorescence in the SERS spectrum, making them feasible for SERS and plasmonic applications. The results also showed that the thin coating does not have adverse effects on the coupling of surface plasmon polariton in AgNW waveguides, and the device performance is stable for at least 21 days. AgNW-AFM probes are low-cost alternatives of high-aspect-ratio, high-resolution AFM probes. It was demonstrated that the Ag@Au core-shell nanowires functions similarly to bare-AgNW, with a much longer shelf-life for at least 3 weeks in the air. The performance of transparent film based on Ag@Au nanowires with 6nm Au can keep stable under heated, high-humidity environment (80 celsius degree of temperature, 80% of humidity) for as long as 2016 hours (>84days).



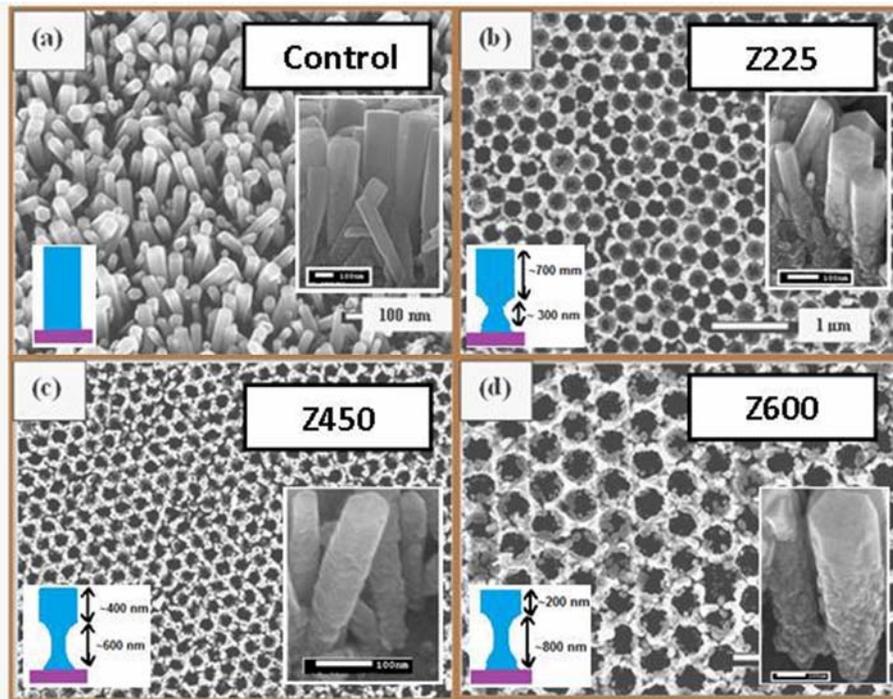
COLL 637

Colloidal particle assisted fabrication of self-cleaning ordered ZnO nanostructures for enhanced room temperature gas sensing by light trapping mechanism

Poulomi Chakrabarty¹, *chpoulomi@gmail.com*, **Meneka Banik**², **Sumita Santra**³, **Narendar Gogurla**³, **Samit Ray**^{4,5}, **Rabibrata Mukherjee**^{6,1}. (1) School of Nanoscience and Technology, IIT KGP, Kolkata, West Bengal, India (2) Chemical Engineering, IIT KGP, Kolkata, West Bengal, India (3) Department of Physics, IIT KGP, Kolkata, West Bengal, India

Bengal, India (4) IIT Kharagpur, Kharagpur, India (5) S N Bose National Centre for Basic Sciences, Kolkata, West Bengal, India

Ordered array of one dimensional (1D) nanostructures have drawn much attention in several applications including antireflection coating, light trapping based optoelectronic devices, electronic communication, sensors, self-cleaning surfaces. Here, we presents the ordered 1D ZnO based nanostructure fabrication using sacrificial transfer printable PS colloidal templates for light induced gas sensing and self cleaning applications. The fabricated ordered ZnO nanorods with a periodic separation of 450 nm shows water contact angle of $\sim 160^\circ$ and contact angle hysteresis of $<5^\circ$, which helps water droplets to clean the accumulated dust and roll off from the surfaces of the samples. The photoconductive and room temperature light induced gas sensing properties of ordered ZnO nanostructures with periodic separation of 225 and 450 nm have studied in comparison to ZnO nanorods without any order (control), under white light illumination with low intensity ($400 \mu\text{W}/\text{cm}^2$) condition. Ordered ZnO nanostructures sensors exhibit an enhanced sensing response upon exposure to NO_x gas in both the conditions of high temperature and light illumination as compared to control ZnO sensor. The enhanced sensing response at high temperature for ordered ZnO sensors is mainly attributed to the increased chemical interactions with NO_x molecules due to porosity nature of nanorods. On the other hand, the ordered ZnO nanorod arrays sensors with separation of 225 nm shows an enhanced response under light activation in comparison to that of nanorods with separation 450 nm and control one. This might be due to the light confinement within the sub-wavelength nanostructures. The optical absorption spectrum of ordered nanorods also confirms the enhanced absorption in the ordered ZnO nanostructures due to light confinement. Our study suggests the effective use of selectively ordered one dimension nanostructures to design the light induced gas sensors operated at room temperature with high sensing response.



COLL 638

Small size Si precursor inhibitors for area-selective atomic layer deposition

Byeong Guk Ko¹, koguk11@gmail.com, **Mohammad Rizwan Khan**¹, **Jae Kwang Lee**¹, **Bonggeun Shong**², **Woo-Hee Kim**³, **Han-Bo-Ram Lee**¹. (1) Materials Science and Engineering, Incheon National University, Incheon, Korea (the Republic of) (2) Chemical Engineering, Hongik University, Seoul, Korea (the Republic of) (3) Division of Advanced Materials Engineering, Chonbuk National University, Jeonju, Korea (the Republic of)

Atomic layer deposition (ALD) is a method of deposition that enables uniform deposition on an atomic basis even in 3D materials. Moreover, area-selective (AS) ALD has been used as a simple patterning process with the several advantages of conventional ALD processes, such as uniformity and excellent conformality. AS-ALD enables the next-generation semiconductor process in 3D nanoscale and in addition, simplifies current fabrication processes. Previously, AS-ALD employed self-assembled monolayers (SAMs) as an inhibitor, which have long tail groups. For high volume manufacturing, however, long chain SAMs can have several disadvantages, such as poor packing quality and long formation time. In this work, we investigated small size of Si precursors as inhibitors i.e., (N, N-dimethylamino) dimethylsilane (DMADMS) and (N, N-dimethylamino) trimethylsilane (DMATMS) to overcome these disadvantages. We deposited the DMADMS via ALD on Si and SiO₂. A hydrophobic surface with a high water contact angle (80°-90°) was observed for DMADMS-coated SiO₂. Adsorption of DMADMS molecules with methyl (-CH₃) tail groups ultimately changes the surface from hydroxyl-(OH)-terminated hydrophilic surface into a CH₃-terminated hydrophobic surface. The DMADMS selectively adsorbs to the OH-terminated areas, and AS-ALD

of metal (Ru) metal oxide (Al_2O_3) was found on part of the surface not covered with the DMADMS molecules i.e. OH-terminated surface. The DMADMS adsorption on SiO_2 was examined with techniques such as surface potential, X-ray photoelectron spectroscopy (XPS), ellipsometry, and density functional theory (DFT) calculation. From surface potential analysis, it was observed that the surface reactivity of SiO_2 is decreased by adsorption of DMADMS, and thus adhesion of DMADMS coated SiO_2 is lower than bare SiO_2 . The present work provides useful information on the design of efficient ALD Si precursors with conformal, and dense, films for area selective growth of metal and metal oxides.

COLL 639

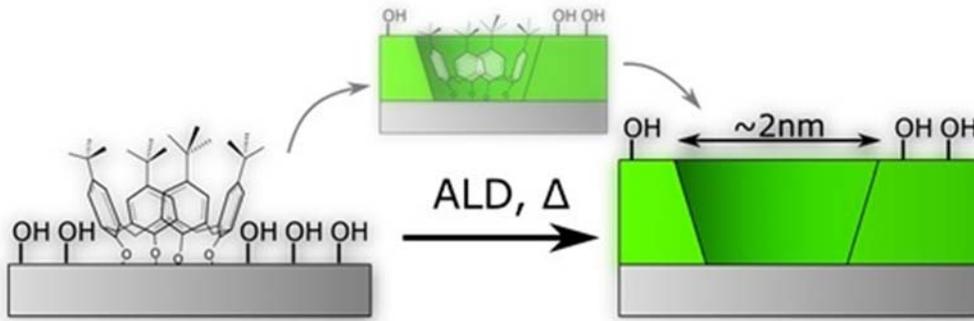
Nanoscale structuring of surfaces by using atomic layer deposition: Controlled synthesis of nanocavities

Christian Hess, hess@pc.chemie.tu-darmstadt.de, Philip Ruff. Chemistry, Technical University Darmstadt, Darmstadt, Germany

Recent advances in nanotechnology enable the fabrication of tailored materials for a variety of applications e.g. in catalysis or alternative energy. In this contribution, we present a novel process for the creation of uniform nanocavities on the surface of nanoporous materials using atomic layer deposition (ALD) and nanotemplate surface patterning (see Scheme). As nanoporous material, we employed silica SBA-15 owing to its large specific surface area and ordered pore structure. To facilitate the grafting of the calixarene nanotemplate, the surface of SBA-15 was pre-treated with an ALD coating of one monolayer of TiO_2 (Ti-SBA-15). The templates were then surrounded by Al_2O_3 as wall material using further ALD treatment. Template removal was achieved at moderate temperatures (60°C) by reaction with ozone preventing damages to the structure. By this approach a homogeneous distribution of uniform nanocavities of conical shape with 1-2 nm diameter, due to the size and geometry of the calixarene template molecules, was obtained.

To elucidate the surface chemistry during nanocavity synthesis, detailed spectroscopic (IR, UV-Vis, and XPS) and microscopic (AFM, TEM) characterization was applied besides thermal analysis. IR and UV-Vis spectra reveal the successful formation of a covalent template-to-substrate binding, which remains unchanged during wall formation but breaks up during ozone treatment. On the other hand, IR spectra confirm that upon grafting the calixarene molecules remain intact. Supporting XPS and TGA measurements give insight into the changing composition of the modified SBA-15 surface and quantification of the amount of grafted template. By using substrates based on planar Si-wafers (SiO_2/Si) the process of nanocavity formation could be directly monitored on a monomolecular level through AFM imaging.

Our results highlight the use of molecule-templated atomic layer deposition (ALD) for the controlled nanoscale structuring of surfaces enabling novel applications in catalysis or alternative energy.



Scheme. Molecule-templated ALD approach for the creation of nanocavities on the surface of nanoporous materials.

COLL 640

TiN etching in the semiconductor industry: Effects of material deposition and etch compositions

*Johan Hoogboom*¹, *johan.hoogboom@basf.com*, *Andreas Klipp*¹, *Lucas Amundson*². (1) G-EDM/NA, BASF SE, Ludwigshafen, Germany (2) G-EDM/EA, BASF Corporation, Hillsboro, Oregon, United States

In the semiconductor industry, titanium nitride is often used as an inorganic hard mask, enabling the robust creation of structures (vias) with widths down to at least 5 nm. After the vias are created, using plasma etching techniques, the hard mask has to be removed again, as its presence during final manufacturing steps would severely impact device performance.

In general, the TiN layer is removed using oxidative etching chemistry. With differentiation between chip manufacturers increasing over the past years, multiple types of TiN are used, mostly differing in deposition technique. These different types of TiN show vastly differing etch rates and underlying mechanisms.

In this paper, we present data on the oxidative etching of TiN, in which the deposition techniques and conditions were varied (PVD, CVD, ALD), as well as the oxidative etching chemistry. We discuss the impact of the deposition technique and composition on the etch rates, film morphology, thermodynamic parameters and underlying mechanisms for various products, and show that tuning of both the TiN film composition and the applied etch product results in a broad range of applicable chemistries which can be used in cutting-edge chip manufacturing technologies.

COLL 641

Probing antimicrobial peptide/lipid A membrane interactions using single-molecule dynamics

Nathaniel Nelson, *nelsonns@colorado.edu*, **Daniel K. Schwartz**. *University of Colorado, Boulder, Colorado, United States*

Antimicrobial peptides (AMP) are a class of polypeptides that are part of the innate immune response in most animals which are particularly effective bactericidal agents against Gram-negative bacteria. These peptides have a vast array of sequences and structures but are typically cationic and between 20-50 amino acids in length. Gram-negative bacterial outer membranes are asymmetric with inner leaflet composed of two-tailed phospholipids and the outer leaflet containing mostly Lipopolysaccharides of which the lipid component is Lipid A. Variations in the structure of Lipid A are thought to give rise to both species bias observed in AMP efficacy as well as AMP resistance seen in certain bacterial strains. In this work we use single molecule microscopy to study the interaction between several species of cationic alpha-helical antimicrobial peptides and supported lipid bilayers (SLB) that mimic the outer membrane of various Gram-negative bacteria. Single-molecule microscopy has allowed for the observation of AMP surface affinity and diffusive mechanisms while interacting with the lipid A SLB. Our findings suggest that AMP molecular dynamics are significantly impacted by subtle changes in the structure of the Lipid A comprising the SLB and that these changes are correlated to the biological efficacy of the AMP.

COLL 642

Analysis of fluorescence recovery after photobleaching for freestanding lipid membrane over SiO₂ microwells

Azusa Oshima¹, *oshima.azusa@lab.ntt.co.jp*, **Hiroshi Nakashima**¹, **Koji Sumitomo**². (1) *NTT Basic Research Laboratories, Atsugi, Kanagawa, Japan* (2) *University of Hyogo, Himeji, Hyogo, Japan*

The lateral diffusion of lipids in artificial membranes is a key factor determining membrane function. Fluorescence recovery after photobleaching (FRAP) is an established technique for obtaining lateral diffusion information. However, the conventional analytical method for determining a diffusion coefficient from FRAP data assumes a sufficiently large uniform membrane. Recently, however, artificial membranes have been frequently combined with micro-structures. We have already reported that a freestanding artificial membrane over microwells is stable and useful for examining the activity of ion channel. In such a case, the freestanding membrane and the supported membrane are combined, and they are not very large. In this study, we adopted a numerical calculation for the FRAP analysis to make it applicable even when the bleached area is small and the artificial membrane is not uniform. In the calculation, the effects of the lateral diffusion during the bleaching process and the divergence of the laser used for bleaching were integrated to ensure that the analysis does not depend on the bleaching conditions. The diffusion coefficient was also treated as a function of the distance from the center of the bleached circle to correspond to a non-uniform artificial membrane. In FRAP experiments for the freestanding membrane over SiO₂ microwells, it showed a complicated recovery curve different from that of the

supported membrane. By comparing it with a numerical calculation, the diffusion barrier at the boundary between the freestanding membrane and the supported membrane could be evaluated. This analysis method will help us to understand membrane function in the nanobiodevice through the fusion of nanotechnology and artificial membrane.

COLL 643

Towards realistic large area cell membrane mimics: Excluding oil, controlling composition and including ion channels

Peter J. Beltramo², pbeltramo@umass.edu, Laura Scheidegger¹, Jan Vermant¹. (1) ETH Zürich, Zürich, Switzerland (2) Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States

Capacitance measurements provide unique insights into the thickness, compressibility, and composition of large area membrane bilayers and are used here in addition to demonstrate the successful incorporation of model ion channels. The simultaneous ability to control the bilayer size and manipulate tension, optically monitor and electrically stimulate free-standing membranes enables precise determination of their specific capacitance and thickness across a wide range of areas. We confirm that membranes formed by this recently developed technique have capacitive properties similar to those formed by existing protocols, including solvent-free approaches, and examine the effect using either hexadecane or squalene as the oil solvent. The results obtained here are relevant for other methods where lipid membranes are reconstituted from a bulk oil solvent. Since biological membranes have a diverse phospholipid profile, we show that the technique can successfully reconstitute membranes with binary composition mixtures. As an outlook, we show the capability for model membrane proteins, specifically α -hemolysin and alamethicin, to be incorporated into the formed bilayers and measure ion transport.

COLL 644

Investigating the interactions of menaquinones with common phospholipids using Langmuir monolayers

*Benjamin J. Peters¹, Cameron Van Cleave¹, Allison Haase¹, Jordan T. Koehn², Katarina Werst¹, Dean Crick¹, **Debbie C. Crans¹**, debbie.crans@colostate.edu. (1) Colorado State University, Fort Collins, Colorado, United States (2) Chemistry, Colorado State University, Fort Collins, Colorado, United States*

Despite quinones from many different organisms have varying structures, they all are thought to move within their respective electron transport systems similarly. All of them are commonly drawn as a circular motion through the bilayer, even though limited information is known about a commonly found electron transporter, menaquinone (MK). MKs with varying lengths of isoprenoid tails have been found across biological systems, and therefore, here we characterize the interactions of MKs with two commonly

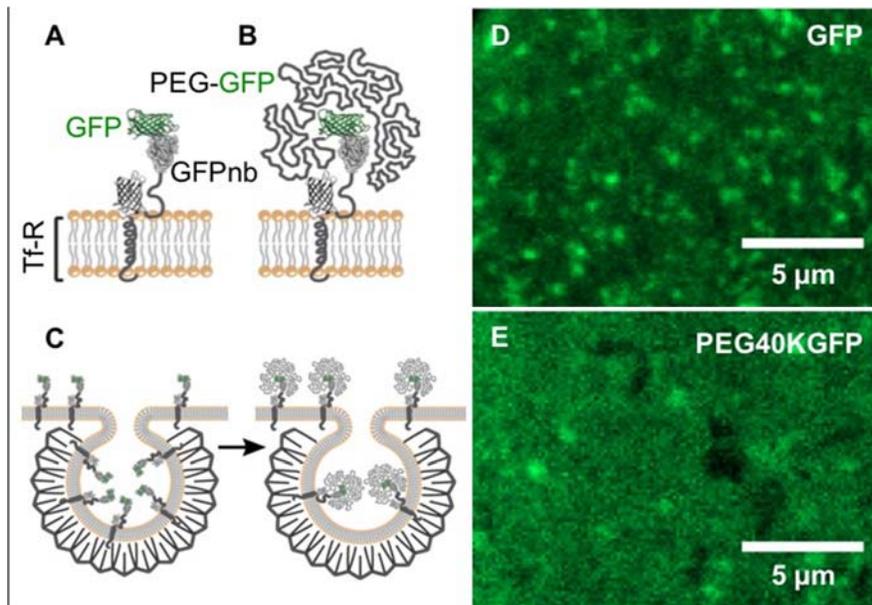
occurring phospholipids, dipalmitoylphosphatidylcholine (DPPC) and dipalmitoylphosphatidylethanolamine (DPPE) using Langmuir monolayer techniques. Compression isotherms were used to characterize pure and mixed monolayers of MKs and phospholipids while Brewster angle microscopy (BAM) was used to further determine the interactions between MK and phospholipids. The compression isotherms were able to show that MK interacts with phospholipid interfaces similarly as ubiquinone and plastoquinone in that as the surface pressure of the monolayers increase, in that they get “squeezed out” of the monolayer onto the phospholipid tails. Using BAM, the aggregation and disappearance of the aggregates were visualized and presented in both pictorial and in graphical interchange format (GIF). The information obtained by this study demonstrates that the interactions of MK with phospholipid interfaces is not only similar to other quinones, but is also a dynamic interaction setting up a basis for computational studies of the dynamics of quinones within bilayers.

COLL 645

Controlling receptor recycling using engineered ligands

Andrea Trementozzi¹, atrementozzi3@utexas.edu, **Andre C. DeGroot¹**, **Chi Zhao¹**, **Jeanne Stachowiak^{1,2}**. (1) Biomedical Engineering, University of Texas at Austin, Austin, Texas, United States (2) ICMB, University of Texas at Austin, Austin, Texas, United States

Cellular responses to stimuli depend on the concentrations of specific receptor proteins at the plasma membrane. These concentrations are determined by a balance between transport of new receptors to the cell surface and removal of old receptors by endocytosis. Therefore, controlling the rate of endocytosis presents a possible strategy for controlling receptor concentrations. It is well understood that receptors are recruited into endocytic structures by recognition of biochemical binding motifs. However, since these motifs are shared by many different receptors, no strategy currently exists for controlling the uptake of individual receptor species. Toward this goal, recent work has demonstrated that biophysical factors can alter uptake rates. Specifically, increasing the physical size of receptors sterically hinders their uptake. In line with these ideas, here we show that binding of a bulky, 40 kDa PEG chain to a model transmembrane receptor (A, B) decreases its uptake rate by a factor of 4. Confocal imaging revealed that the model receptor-ligand complex localized within endocytic pits (D). In contrast, localization was reduced upon addition of the large ligand, indicating diminished endocytic uptake (E). These results demonstrate the ability to control receptor internalization, thereby retaining specific receptors on the plasma membrane surface. This biophysical approach for manipulating receptor uptake is a key first step towards developing a precise method for controlling the cellular response to activation of specific receptors of biologic and therapeutic significance.



(A) Model transferrin (Tf-R) receptor with GFP as the ligand. (B) PEG-GFP increases overall size of ligand-receptor complex. (C) Reduced uptake into endocytic structures occurs due to steric hindrance from the bulky PEG. (D) Clear punctate structures from confocal imaging at the cell plasma membrane indicate ligand-receptor complex uptake into endocytic structures. (E) Loss of clear puncta demonstrate reduced uptake into endocytic structures.

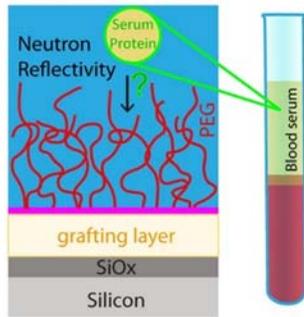
COLL 646

Neutron reflectometry reveals structural aspects of blood protein and antibody adsorption to polymer brushes

Victoria M. Latza¹, victoria.latza@mpikg.mpg.de, **Ignacio Rodriguez Loureiro**¹, **Irena Kiesel**², **Avraham Halperin**³, **Giovanna Fragneto**⁴, **Emanuel Schneck**¹. (1) Biomaterials, Max-Planck-Institute for Colloids and Interfaces, Potsdam, Germany (2) TU Dortmund, Dortmund, Germany (3) Université Joseph Fourier, Grenoble, France (4) Institut Laue Langevin, Grenoble, France

Poly[ethylene glycol] (PEG) brushes are reputed for their ability to prevent undesired protein adsorption to material surfaces exposed to biological fluids. Protein adsorption to biomedical surfaces is a major issue of this technology because it can lead to harmful foreign body reactions. However, numerous cases where the PEG brush approach failed have been reported and further investigation of the underlying molecular mechanisms is required. Here, we performed experiments to characterize the adsorption of proteins from blood serum and of two types of anti-PEG antibodies to poly(ethylene glycol) (PEG) brushes grafted to planar phospholipid surfaces. In order to obtain protein and PEG concentration profiles as a function of the altitude, we use neutron reflectometry (NR). The measurements yield volume fraction profiles of lipid head groups, PEG, and adsorbed proteins at sub-nanometer resolution. For whole human blood serum the reflectivity curves show significant primary adsorption into the

lipid head group region and suggest the presence of a low amount of ternary adsorption at the brush periphery. In context with anti-PEG antibodies we obtained qualitatively different results for antibodies binding specifically to the PEG end points (endbinders) and to the backbone (backbonebinders) of the polymer. For endbinders the adsorbed amount of antibodies increases with brush grafting density, whereas backbonebinders exhibit a non-monotonic behavior. The results may constitute the basis for future applications of PEG brushes with enhanced biocompatibility.



Scheme of the PEG brush functionalized model system; the adsorption of proteins to the surface was monitored with neutron reflectometry

COLL 647

Label-free direct visualization of multivalent binding of cartilage oligomeric matrix protein and bone morphogenetic protein-2

Victoria Tran¹, vktran@ucdavis.edu, **Arpad Karsai**¹, **Michael Fong**², **Qingbo Yang**¹, **Jasper Yik**², **Dominik Haudenschild**², **Gang-Yu Liu**¹. (1) Department of Chemistry, University of California, Davis, California, United States (2) Department of Orthopaedic Surgery, University of California Davis Medical Center, Sacramento, California, United States

Bone morphogenetic protein-2 (BMP2) enhances osteogenic differentiation of bone progenitor cells. However, BMP-2 treatment has not been utilized extensively for bone repair and regeneration due to severe side effects caused by the large dosage of the protein required. Cartilage oligomeric matrix protein (COMP) is a non-collagenous homopentameric protein found in the extracellular matrix of cartilage, ligaments, and tendons. Prior studies have reported that stimulating progenitor cells with COMP and BMP2 mixture greatly enhanced osteogenesis. This presentation aims at providing structural evidence at the molecular level that COMP binds BMP2 molecules via multivalent interactions. High resolution atomic force microscopy (AFM) enables visualization of the conformation of COMP, mostly in a pentameric form. In addition, AFM topographic images reveal the number and location of BMP-2 bound on a COMP molecule. This is the first direct and label-free evidence that BMP2 bound to the C-terminal domains of COMP. These findings, in conjunction with cellular osteogenesis assays, provide new insights on how molecular level presentation of growth factors

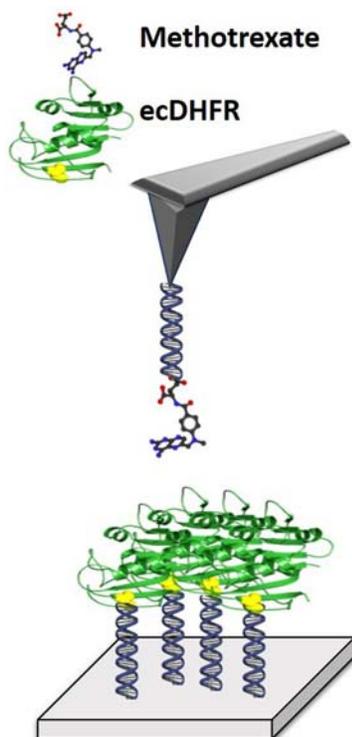
impacts the downstream cellular signaling processes to enhance cellular differentiation for bone growth and regeneration.

COLL 648

Single molecule level studies of enzyme-ligand interactions using molecular recognition atomic force spectroscopy

Thiranjewa I. Lansakara, thiranjee-lansakaramudiyanselage@uiowa.edu, Holly Morris, Priyanka Singh, Amnon Kohen, Alexei V. Tivanski. Chemistry, The University of Iowa, Iowa City, Iowa, United States

Single molecule level studies can lay the foundation towards understanding the microscopic nature of interaction forces between ligands and enzymes that in turn strongly influence majority of biological processes. Study of interactions between individual molecules is not accessible from experiments utilizing a large ensemble of molecules. Such information is important since the averaged properties may not truly represent the single molecular responses. This study utilizes high spatial and force resolution provided by the Atomic Force Microscopy (AFM) under physiological conditions to quantify the force-distance information of enzyme-ligand interaction. Different immobilization techniques were utilized to chemically bind the enzyme to the surface and ligand molecules to the AFM tip and then results were quantitatively compared to improve the accuracy and reproducibility of the measurements. Measurements of forces required to rupture enzyme-ligand complex were carried out on directly immobilized enzymatic monolayer and compared with enzymes bound to surface through a rigid double stranded (ds) DNA spacers. Ligand molecules were attached to the tip via either flexible polyethylene glycol or rigid dsDNA linkers. This 123-base pair containing 41 nm long rigid dsDNA linker was proved to withstand repetitive force measurements of enzyme-ligand rupturing. The findings of this study indicate that new single molecule approach for measuring enzyme-ligand interactions based on rigid dsDNA linker on both tip and surface afford highly specific and accurate force measurements.



COLL 649

Surface-enhanced Raman spectroscopy of fluid supported lipid bilayers on silica-coated silver film over nanosphere structures

Ian Bruzas, ibruzas74@gmail.com, Laura Sagle. Chemistry, University of Cincinnati, Cincinnati, Ohio, United States

Raman spectroscopy has a long history of use in characterizing artificial and biological membranes. This is due to the capability for direct molecular identification and rich structural information that can be obtained with Raman spectroscopy. Supported lipid bilayers are an essential biomimetic system that have been used for fundamental analysis of biological membranes and membrane-based sensor development. With few exceptions Raman spectroscopy and supported lipid bilayers are largely incompatible as Raman scattering suffers from poor efficiency. Surface-enhanced Raman scattering (SERS), however, is a well-developed ultrasensitive technique that allows for orders of magnitude signal enhancement for molecules spatially located near nanometric metal surfaces. Fluid lipid bilayers are challenging to characterize with SERS due to their incompatibility with bare metal surfaces and the difficulty of preparing a thin biocompatible layer that retains lipids within the rapidly decaying enhanced electromagnetic fields. Here we demonstrate a method for reliably coating a silver film-over-nanosphere structure with an ultrathin silica film using a silica sol-gel technique for SERS characterization of fluid supported lipid bilayers. Kinetics of deuterium labelled lipid exchange and measurement of small molecule intercalation into the lipid bilayer are shown in addition to substrate characterization.

COLL 650

Near infrared electrochemiluminescence of Au nanoclusters: Solution sensing and surface assays

Gangli Wang¹, glwang@gsu.edu, **Tanyu Wang**¹, **Hedi Ma**¹, **Shuang Chen**^{1,2}. (1) Department of Chemistry, Georgia State University, Atlanta, Georgia, United States (2) Chemistry, Anhui University, HeFei, China

Near IR luminescence from Au-thiolate nanoclusters is beneficial for analytical applications that require low background interference to achieve high contrast or S/N ratio. In parallel to the photo activation, like fluorescence excited by light source, redox reactions with either electrodes or redox species can provide activation energy and generate electrochemiluminescence (ECL) or chemiluminescence. The simplified instrumental aspects are advantageous for broader applications in resource limiting situations. This talk will discuss the enhancement in the near IR ECL from AuNCs by Good's pH buffer HEPES and related sensing strategies. HEPES as representative piperazine derivative drugs or metal ions are demonstrated to modulate the ECL signals as prototype analyte. Generalizable strategies and detection platforms will be discussed in both solution diffusion pathways and surface assembly of AuNC films.

COLL 651

Luminescent group IB alloy metal nanoclusters with atomic precision

Haizhu Yu, yuhaizhu@ahu.edu.cn, **Manzhou Zhu**. Anhui University, Hefei, China

Ultrasmall metal nanoclusters (with size < 2 nm) have recently attracted increasing research interest, thanks to their superior molecular-like physical-chemical properties (such as the discrete frontier orbitals, photoluminescence and chirality). Specifically, in recent years, different strategies, such as ligand engineering, metal doping, aggregation induced emission (AIE) and crystallization induced emission enhancement (CIEE) have been successfully explored to enhance the photoluminescence of metal nanoclusters. Benefiting from the small size, uniform morphology, optical-stability and biocompatibility, the luminescent nanoclusters have shown highly attractive applications in bio-imaging and sensing.

Aggregation represents one of the most efficient strategies to enhance the emission intensity, predominantly because of the restriction of non-radiative rotational and vibrational motions. Motivated by this fundamental idea, our group recently prepared a series of Au-Cu and Au-Ag alloys, using either the chemical bonding or noncovalent interaction induced aggregation. We first endeavored to prepare a series of Au₂Cu₆(PR₃)(SR)₆ nanoclusters via a novel AIE strategy, which was achieved by controllable aggregation of the chemically active Cu(I) complexes with the chemically inert Au(0) atoms under reducing environment. As the luminescence originates from the phosphine ligand to metal charge transfer, the enhancement of emission intensity has been achieved by introducing strong electron-donating substituents on the phosphine

ligands. Distinct from the Au-Cu bonding interaction induced aggregation, we also synthesized a luminescent Au-Ag alloy (i.e. $\text{Au}_4\text{Ag}_{13}(\text{PPh}_2\text{CH}_2\text{PPh}_2)_3(\text{SR})_9$), which exhibit strong luminescence in crystalline state, while very weak emission in both amorphous and solution state. With the aid of density functional theory calculations and careful structural analysis, we found that the unusual CIEE phenomenon was mainly caused by the compact noncovalent C-H... π interactions between exterior ligands of the neighboring nanoclusters.

COLL 652

Single molecule conductance of ferrocene on gold

Maria Kamenetska, *mkamenet@bu.edu*. *Chemistry and Physics, Boston University, Boston, Massachusetts, United States*

The motivation to probe chemical structure and function on the single molecule level is driven both by technological challenges and the need for deeper mechanistic understanding. In particular, to realize the vision of single molecule electronics, we need to understand how atomic level structure of a metal-molecule-metal junction affects electron transport. Here, we use a home-built Scanning Tunneling Microscope Break Junction (STMBJ) technique to probe the structure and conductance of single ferrocene molecules functionalized to bind to gold electrodes. We show that the choice of chemical linker-groups affects transport characteristics because binding configurations influence electronic properties of the junction.

COLL 653

Discovery of biomaterials by simulation and experiment: Molecular recognition, assembly, applications

Hendrik Heinz, *hendrik.heinz@colorado.edu*. *Department of Chemical and Biological Engineering, University of Colorado-Boulder, Boulder, Colorado, United States*

The discovery of functional biomaterials remains largely driven by serendipitous trial-and-error studies, whereby the rational understanding and design using modeling and simulation play an increased role thanks to more affordable computing resources and more accurate models. This talk describes simulation techniques and their capabilities at the 1 to 1000 nanometer scale and molecular recognition mechanisms on metals, oxides, and biominerals (apatites). Applications to nanocrystal growth, catalyst design, hydrogels, and therapeutics are shown. The mechanism of specific adsorption and assembly of peptides and biomacromolecules onto metallic and oxidic nanostructures will be described according to measurements and simulations with novel force fields and surface models. Thereby, differences in surface energy the diversity in surface chemistry are found to play a major role, as illustrated for silica and apatites where changes in pH lead to similarity scores of attracted peptides lower than 20%. Possible controls and design principles are explained.

COLL 654

Controlled dopant speciation of dopants in CdS-based nanoclusters

Kevin R. Kittilstved, kittilstved@chem.umass.edu. Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States

The precise control over the location of targeted dopants using expensive and time-consuming vacuum deposition techniques revolutionized the semiconductor industry. However, the analogous level of precision has not been attained in the solution-based syntheses of semiconductor nanostructures. The nucleation and growth kinetics of nanocrystals from monomeric precursors strongly favors the nucleation of undoped cores with dopants only incorporated during growth. As an alternative strategy to introduce dopants in the critical nucleus, we have focused our studies on a class of discrete molecular clusters that possess a framework similar to zincblende CdS. In this talk, we will present recent studies on the controlled speciation of transition metal ions into the core or surface cation sites of both $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ and $[\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}]^{2-}$ clusters. Confirmation of cluster location in the cluster is deduced from electrospray ionization mass spectrometry and various spectroscopies including electronic absorption and photoluminescence. These results provide insight into how the cluster dynamics and cluster-to-cluster equilibria can be exploited to introduce and trap impurities in the cluster core.

COLL 655

Probing phase evolution of metal oxide nanomaterials in batteries

Dong Su^{1,2}, dsu@bnl.gov. (1) Brookhaven National Laboratory, Upton, New York, United States (2) Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States

For developing new generation nanomaterials for energy applications, the understanding of the factor/mechanism governing their performance is of primary importance. Advanced (scanning) transmission electron microscopy ((S)TEM) techniques have recently been developed to investigate the relationship between the nanomaterials' structure and their functions, with the help of combined electrochemical and theoretical approaches. In this talk, I will discuss how to use advanced TEM techniques to characterize the redox reaction of the transition metal oxide nanoparticles for lithium ion batteries. While *ex situ* TEM study reveals the structural change in the real cell and probe local phase, interfacial and chemical information at an atomic resolution, *in situ* TEM study can help us to understand the phase evolution in real time. In the case of spinel oxides nanoparticles, Fe_3O_4 and Co_3O_4 , we have observed the competition between intercalation and conversion reactions in non-equilibrium state. Surprisingly, these two reactions can be co-existed within one single particle. Phase-field simulation reveals that the reaction pathway is governed by the rate of lithium

diffusion. This talk highlights the unique capability of combining *in situ* TEM with theoretical simulation to investigate the mechanisms of redox reaction.

COLL 656

Nano catalyst with enhanced activity and stability

Tao Li^{2,1}, tli4@niu.edu. (1) Advanced Photon Source, Argonne National Lab, Lemont, Illinois, United States (2) Chemistry & Biochemistry, Northern Illinois University, DeKalb, Illinois, United States

Carbonaceous feeds, such as oil, gas, and coal, can be catalytically converted to useful products. Many of these reactions are conducted under harsh conditions, where the metal catalysts will rapidly sinter and the reactivity is reduced quickly. It has been shown that overcoating the metal nanoparticles with alumina using atomic layer deposition (ALD) will reduce the sintering and if the overcoated particles are thermally treated at high temperatures, the lifetime and reactivity of catalyst increase dramatically compared to the catalyst without ALD overcoating. It is believed that nano-sized pore (less than 2 nm) was formed during the calcination. However, the mechanism of pore formation is still poorly understood due to the limited characterization technique.

Understanding the mechanism of the pore formation and further controlling the pore size are crucial for the development of the ALD overcoated catalyst. Recently, it is demonstrated that small angle X-ray scattering (SAXS) is very powerful technique to characterize these ALD overcoated catalysts. From SAXS analysis, it was found that the thermal treatment resulted in the formation of ~ 3.5 nm pores, which agrees with the BET results. Moreover, the evolution of pore size was monitored by *in situ* SAXS technique. The pore size increases with increasing annealing temperature. In this talk, we will talk about our recent results of investigating the mechanism of pore formation during the calcination using *in situ* SAXS as well as wide angle X-ray scattering, to understand how the ramping rate, gas used, nature of supports and overcoated materials affect the formation of the pore.

COLL 657

Watching single nanocrystal transformations with fluorescence microscopy

Bryce Sadtler^{1,2}, sadtler@wustl.edu, Bo Yin². (1) Department of Chemistry, Washington University in Saint Louis, Saint Louis, Missouri, United States (2) Institute of Materials Science & Engineering, Washington University in St. Louis, Saint Louis, Missouri, United States

Nanoscale crystals provide model systems to understand the complex kinetics of solid-state transformations. For example, the conversion of lead iodide into methyl ammonium lead iodide involves the intercalation of both a methyl ammonium cation and an iodide anion along with a change in the connectivity of the lead iodide octahedra.

This solid-state reaction is one route to produce polycrystalline perovskite semiconductor films for photovoltaic devices, where the grain size and surface faceting of the perovskite films strongly affect device performance and stability. We are using single-particle fluorescence microscopy to directly observe this transformation in crystals with sizes of 10 nm or less. By monitoring the reaction kinetics of hundreds of nanocrystals, we propose a model for this solid-state transformation in which initial intercalation events at the surface activate the nanocrystal for rapid and complete transformation.

COLL 658

Partially poisoned Pd nanoparticles for selective hydrogenation and/or isomerization of olefins

Mohammed Mahdaly¹, Kevin M. Vargas², Young-Seok Shon^{2,3}, ys.shon@csulb.edu. (1) Chemistry and Biochemistry, California State University Long Beach, Long Beach, California, United States (2) Department of Chemistry and Biochemistry, California State University, Long Beach, Long Beach, California, United States (3) Keck Energy Materials Program, California State University Long Beach, Long Beach, California, United States

Selective hydrogenation and/or isomerization of olefins are important processes in both chemical and pharmaceutical industries. Our group previously reported that the thiosulfate protocol using sodium S-alkylthiosulfates instead of alkanethiols could generate catalytically active Pd nanoparticles (PdNPs) capped with a lower density of alkanethiolate ligands. PdNPs were characterized by thermogravimetric analysis (TGA), proton NMR, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), IR and UV-vis spectroscopy, and gas adsorption using the Brunauer-Emmett-Teller (BET) model. These unsupported colloidal PdNP catalysts exhibit an excellent selectivity toward the isomerization of allylic alcohols to carbonyls in organic solvents. PdNPs are also found to have high selectivities for the isomerization of terminal alkenes to internal alkenes and the mono-hydrogenation of dienes and trienes. High chemoselectivity for the hydrogenation of olefins in the presence of other reactive functional groups such as nitro, halo, nitrile, imine, and carbonyl groups is observed for the partially poisoned colloidal nanoparticles. The high activity of colloidal Pd nanoparticle catalysts allows the reactions to be completed under mild conditions, at atmospheric pressure and room temperature. In addition, these homogeneously soluble PdNP catalysts offer an advantage of facile separation and multiple recycling without significant losses in activity and selectivity. The strong influence of thiolate poisoning ligands on the chemical and electronic properties of the Pd surface is observed from various catalysis results. The further systematic evaluation of metal nanoparticle catalysts functionalized with well-defined small thiolate ligands would provide important fundamental understandings on the influence of chemical environments near active sites and pave a way to develop chemo-, regio-, and stereo-selective colloidal nanoparticle catalysts.

COLL 659

***In-situ* visualization of plasmon-induced hydrogenation reactions in individual palladium nanocubes**

Michal Vadai¹, michalva@stanford.edu, Daniel K. Angell¹, Fariah hayee¹, Katherine Sytwu², Jennifer A. Dionne¹. (1) Stanford University, Stanford, California, United States (2) Stanford Univerity, Stanford, California, United States

Plasmonic nanoparticles are emerging as a new class of photocatalysts due to their ability to efficiently absorb light and convert it into chemical energy. Compared to traditional semiconducting photocatalysts, plasmonic nanoparticles offer additional routes to improve reactivity, including electromagnetic field enhancement, localized heating and efficient hot carrier excitation. While these effects have been exploited to increase the efficiency of numerous reactions, it remains unclear how the underlying plasmonic excitations affect multi-step reaction kinetics and promote site-selectivity. In particular, most measurements are conducted on particle ensembles, where correlating the reaction dynamics with local structural features is not possible. Single particle measurements help disentangle structure-function relations, but to date only very few such studies exist and all lack the requisite spatial and temporal resolution to directly observe chemical transformations and their associated reaction pathways within a nanoparticle.

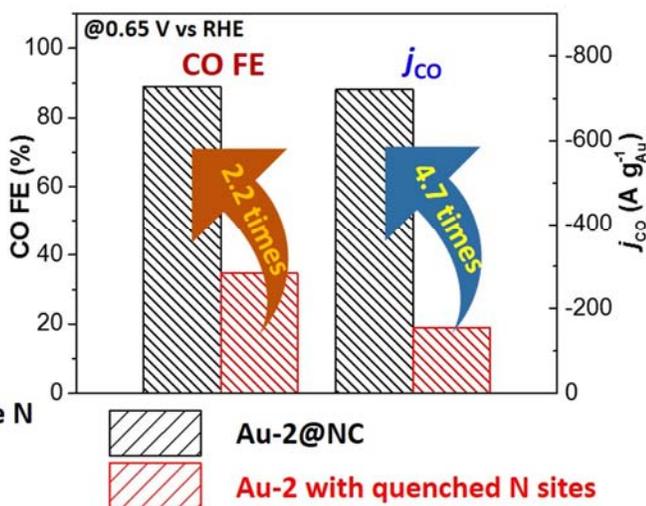
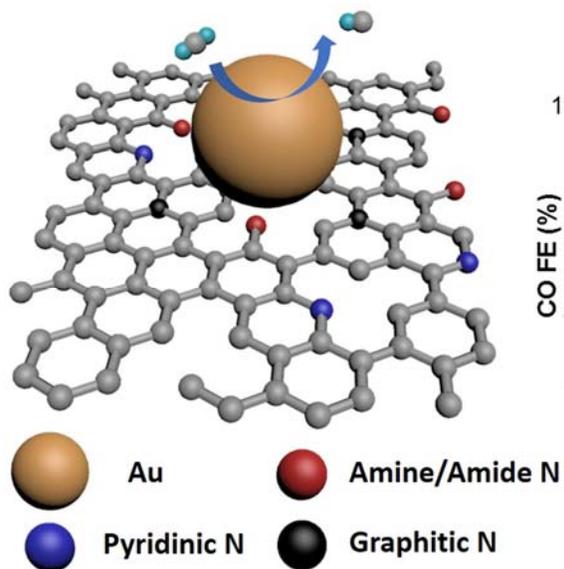
Here, we visualize a plasmon-induced phase transformation reaction at the single and sub-nanoparticle level in-situ and in real-time. Using an environmental transmission electron microscope (ETEM) combined with light excitation, we study the photocatalytic dehydrogenation of individual palladium nanocubes coupled to gold nanoparticles; in this configuration, the palladium nanocubes serve as reactors for the dehydrogenation reaction, while the gold nanoparticles serve as efficient visible-light harvesters. A combination of electron diffraction, electron energy loss spectroscopy, and direct imaging provides sub-2nm spatial resolution of the light-induced transformation. We observe two main reaction steps in the dehydrogenation transformation and show that plasmons enhance the reaction rate of these steps in distinct ways, with a more than ten-fold increase in total rate compared to the dark reaction. Additionally, we find that plasmons enable a new phase transformation mechanism that is not observed without illumination. We also show that phase nucleation occurs more often at electromagnetic hot-spots, demonstrating the contribution of plasmons to site-selectivity. The unique capabilities of a combined high resolution TEM and external illumination allow us to study photo-induced reactions in an unprecedented resolution, en-route to design of site-selective and product-specific photocatalysts.

COLL 660

Superiorly active and selective Au nanocatalysts supported on nitrated carbon for electrocatalytic CO₂ reduction

Lei Jin¹, lei.jin@uconn.edu, Ben Liu¹, Pu Wang², Huiqin Yao¹, Laura Achola¹, Peter Kerns¹, Aaron Lopes¹, Yue Yang¹, Joshua Ho³, Alexander Moewes³, Yong Pei², Jie He¹. (1) Department of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Department of Chemistry, Xiangtan University, Xiangtan, Hunan, China (3) Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

Due to the increased environmental threat from CO₂ emission, efficient and selective conversion of CO₂ to useful chemicals and fuels has received considerable attention. Developing new nanocatalysts is an attractive solution. Of various catalysts explored to date, gold (Au) is the most promising one to convert CO₂ to CO in an aqueous-phase electrochemical reduction. However, ultrasmall Au nanocatalysts (AuNCs, < 2 nm) have proven to be more favorable for water reduction over CO₂, although they possess a large surface-to-volume ratio providing abundant active sites. We report that ultrasmall AuNCs (1.9 ± 0.3 nm) supported on nitrated carbon showed remarkable activity and selectivity for CO₂ reduction. At 0.7 V, the mass activity reaches > 1000 A g⁻¹ with a Faradaic efficiency for CO of ~80 %, that is an order of magnitude more active than the state-of-the-art results. The cooperative effect of Au and the nitride carbon support is essential for the high activity and selectivity of ultrasmall AuNCs. X-ray photoelectron spectroscopy (XPS) shows an electron rich surface of AuNCs on nitrated carbon, compared to the ones after quenching N sites. Thermogravimetric analysis/mass spectrometry (TGA-MS) confirms that the nitrated carbon has a stronger CO₂ adsorption compared to the ones with quenched N sites. We expect that our results will illustrate an alternative way to effectively lower the cost of Au catalyst per unit weight of the product while maintaining the high selectivity for CO₂ reduction.



COLL 661

Plasmonic photocatalytic silver nanoparticles for hydrogenation and oxidation reactions

Alexandra Gelle¹, alexandra.gelle@mail.mcgill.ca, **Michael J. Landry**², **Audrey H. Moores**³. (1) Chemistry, McGill University, Montreal, Quebec, Canada (2) Chemistry, McGill University, Montreal, Quebec, Canada (3) Chem Dept, McGill University, Montreal, Quebec, Canada

Colloidal solutions of Cu, Ag and Au NPs exhibit bright colors due to their unique optical properties called localized surface plasmon resonance (LSPR). When plasmonic nanoparticles (PNPs) are irradiated, their electron cloud is being displaced by its interaction with the electric field component of light, creating surface charges, negative where there is an excess of electrons and positive where the electron cloud lacks. This creates a restoring force, associated with a resonance frequency, typically corresponding to absorption in the visible to near infra-red regions. Therefore, plasmonic nanoparticles are exciting and promising candidates for light-activated catalysis.

Activation of hydrogen on silver nanoparticle usually require high pressure and temperature as previously reported by several groups. Excitation of hot electrons by LSPR was hypothesized to be an appealing avenue to overcome this limitation. LSPR generated hot electrons are known to transfer to adsorbed substrate to induce chemical reactivity. PNPs with sharp vertices are well-known to create “hot spots” where LSPR is greatly enhanced. Plasmonic silver nanocubes (Ag NCs) were developed herein as catalysts for the activation of molecular hydrogen and the hydrogenation of ketones and aldehydes via visible light irradiation at only 1 atm of molecular hydrogen. Oxidation of aldehydes to carboxylic acid in air was also demonstrated.

We report herein the use of plasmonic silver nanocubes (Ag NCs) for the activation of molecular hydrogen and the hydrogenation of ketones and aldehydes via visible light irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes, at 80 °C. 1 atm of molecular hydrogen is required to access, using catalytic amounts of silver, primary, and secondary alcohols, with complete chemoselectivity for C=O over C=C reduction. The mechanism proposed follows a Horiuti-Polanyi scheme, with dissociation of gas resulting from hot electron transfer to the antibonding orbitals of hydrogen gas.

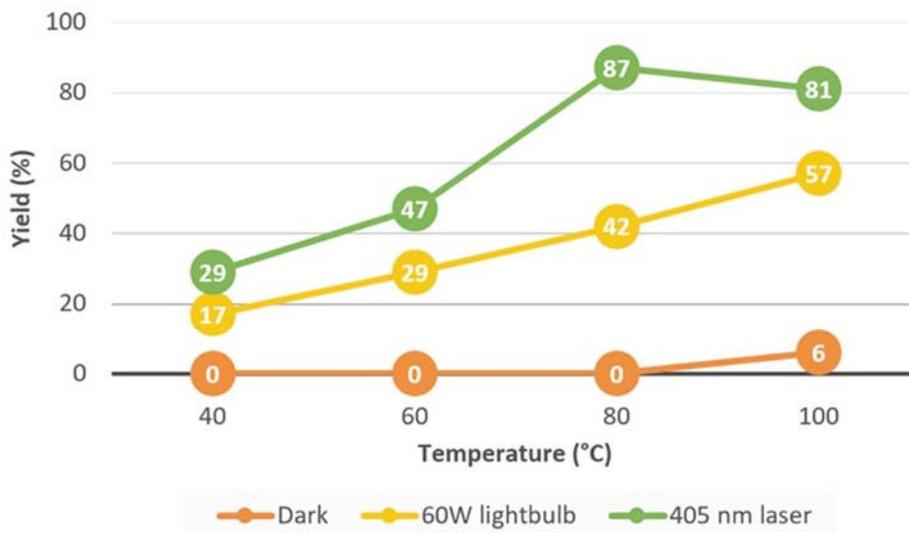


Figure 1. Yields observed for the hydrogenation of camphor with Ag NCs as catalyst. Reaction conditions: 1 mg of Ag NCs, 1 mmol of camphor and 5 mL of dioxane, H₂ pressure of 1 atm, 24 h.

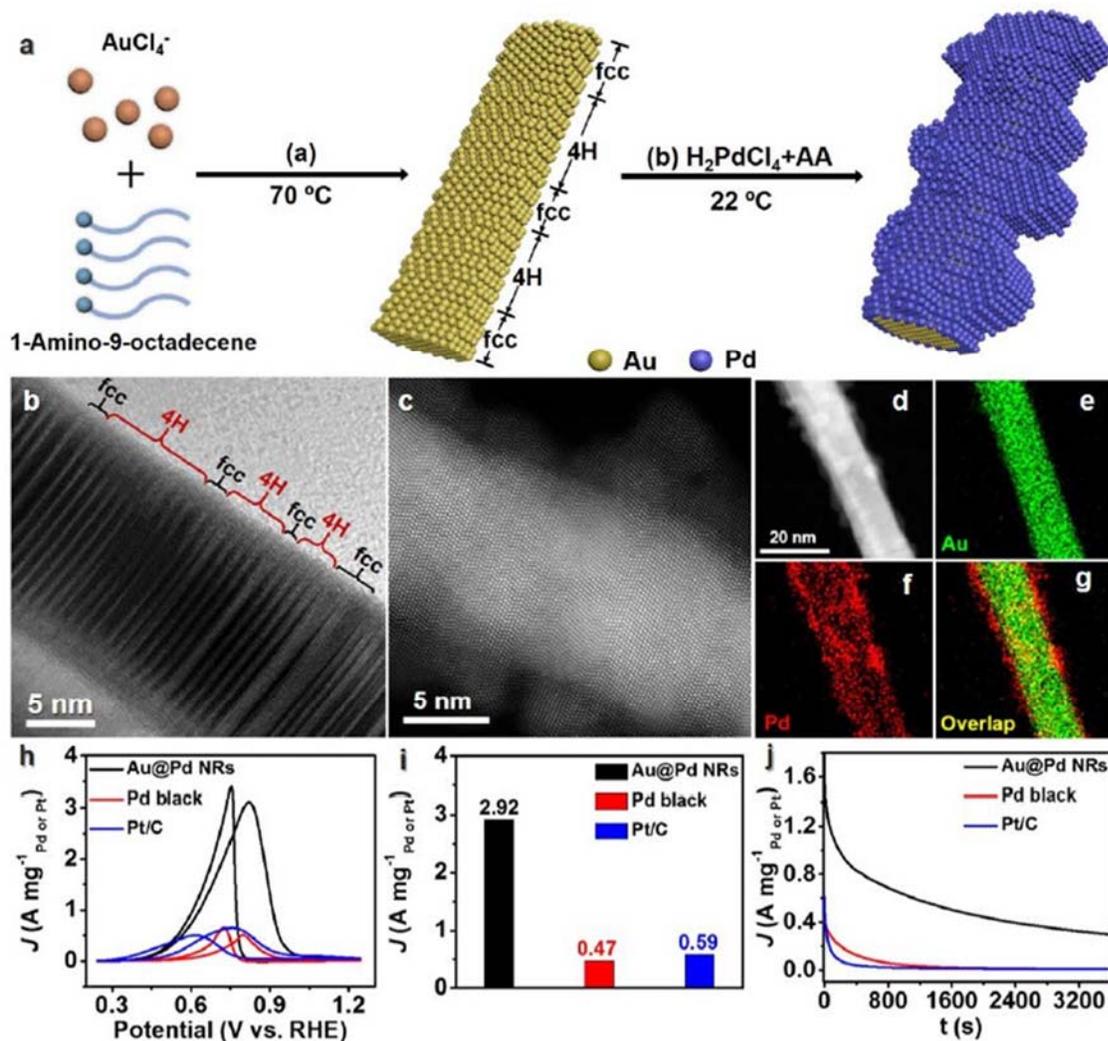
COLL 662

Colloidal synthesis of noble metal nanostructures with unusual crystal phase

Ye Chen, chen1023@e.ntu.edu.sg, Zhanxi Fan, Hua Zhang. *Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore*

Noble metal nanomaterials are outstanding catalyst candidates due to their excellent intrinsic catalytic activities, high conductivity and high stability. While traditional solution-based syntheses mostly focused on shapes, sizes and compositions of the nanocrystals, we made some discoveries on crystal phase controlled wet-chemical synthesis. In this presentation, our recent discovery on the crystal phase-controlled synthesis of noble metal structures is summarized. First, we introduce the first-time synthesis of Au nanorods with alternating 4H and face-centered-cubic (*fcc*) crystal phases, i.e. an unconventional 4H/*fcc* crystal-phase heterostructure, via a one-pot high-yield colloidal approach. Second, epitaxial growth of electrocatalytically active Pd on 4H/*fcc* Au nanorods to form Au@Pd core-shell heterostructures is demonstrated. This unreported metastable phase serves as an excellent substrate on which other catalytically active metals can be grown epitaxially in 4H phase. Last but not the least, the resultant heterostructures containing novel 4H phase show excellent properties in electrochemical catalysis. The superior catalytic performance of crystal-phase-heterostructured 4H/*fcc* Au@Pd core-shell nanorods towards ethanol oxidation reaction is demonstrated. Specifically, the superior mass activity of 4H/*fcc*Au@Pd nanorods was measured to be 6.2 and 4.9 times those of commercial Pd black and Pt/C catalysts, respectively. The study on the metastable phases can lead to novel physical or chemical properties of the noble metals. Our work provides an alternative strategy to

engineer the crystal phase of noble metal nanomaterials via wet-chemical method and explore their templating effects on various properties.



COLL 663

Equilibrium and transport distributions of DNA in hydrophilic nanotubes

Fernando Cruz, fjalacruz@yahoo.co.uk, **Jose Mota**. *Universidade NOVA de Lisboa, Caparica, Portugal*

Hamiltonian-biasing techniques spanning a sub- μ s timescale reveal that, in the presence of an electric field acting upon single-walled carbon nanotubes (SWCNTs), encapsulation of a DNA dodecamer occurs with fast kinetics (≤ 4.3 ns) and is thermodynamically spontaneous (~ 40 kJ/mol). Encapsulation is driven by strong electrostatic attractions between the nucleic acid and the solid, which in the early stages of confinement accounts for at least 80 % of the total interaction energy. The encapsulated DNA length is similar to that of the canonical B-form (3.8 nm) in the two

solid topologies under consideration, (51, 0) and (40, 0); however, consecutive free-energy minima occur in the thermodynamical landscapes, corresponding to a 0.25–0.5 nm deviation from the canonical form (Fig. 1). By contrast with the larger (51,0) topology, the Φ_2 phase space spans a broader range now including non-stable (transient) highly compressed DNA forms ($\Phi_2 < 3$ nm).

The effects exerted by the confining solid exhibit a marked dependence on nanopore diameter, attributed to entropic reasons arising from free-volume considerations. DNA maintains translational mobility within a cylindrical volume comprised between *termini*, according to an anisotropic self-diffusion mechanism involving a self-rotation of the double-strand axis ($v^{max} \approx 27$ m/s).³

Precise physiological conditions (310 K, [NaCl]=134 mM) allow the extrapolation of results to *in vivo* systems and constitute a novel and thorough contribution to nanotube technology in the areas of nucleic acid encapsulation/delivery and personalized therapeutics.

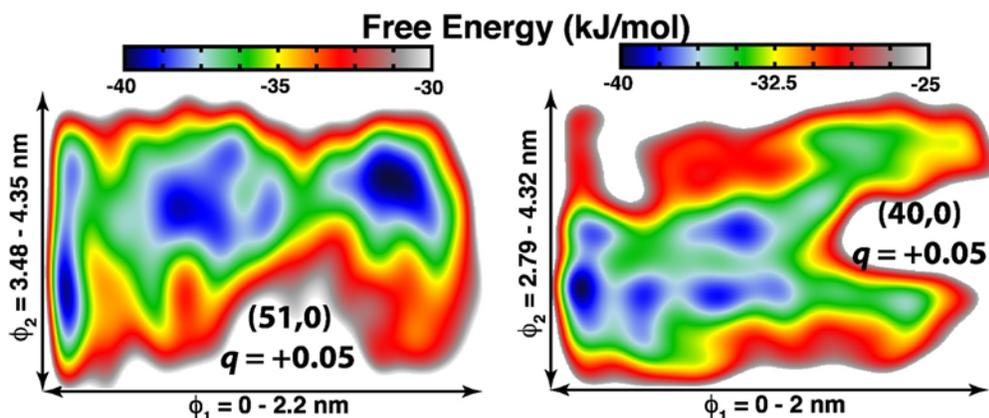


Fig. 1 Free-energy maps of DNA@SWCNT. Φ_1 is the distance between centres of mass of DNA and the SWCNT, projected along the nanopore's main axis (z), and Φ_2 corresponds to the DNA length. Low-lying free-energy valleys are distributed along the nanopore endohedral volume, $\Phi_1 < 2$ nm, and linked amongst themselves via a thermodynamical highway with a free-energy penalty ≤ 5 kJ/mol.

COLL 664

Understanding and characterizing lipid bilayer dynamics by vibrational sum frequency generation spectroscopy

Azhad Chowdhury¹, cazhad@hotmail.com, Fangjie Liu², Minh Phan³, Frederick Heberle^{4,5}, John Katsaras⁴, Charles P. Collier², Ying-Zhong Ma¹, Benjamin Doughty¹. (1) Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (2) Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (3) Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (4) Large Scale Structures Group, Neutron Sciences Directorate and Shull Wollan Center: A Joint Institute for Neutron Science, Oak Ridge National Laboratory, Oak Ridge,

Tennessee, United States (5) Joint Institute for Biological Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States

In cellular membranes, the transbilayer movement of phospholipids between the inner and outer leaflets regulates many cellular activities such as growth, shape, and cellular signaling. Until recently, this lipid translocation or “flip-flop” was believed to be primarily a protein-mediated process, and only more recently has evidence accumulated that relatively rapid flip-flop is possible even without proteins. Despite the evidence for flip-flop in lipid-only model systems, the mechanisms driving this process are unclear, and even less is known about how the addition of other common chemical species—for example, those that induce domain formation—might impact the flip-flop dynamics, or the partitioning of lipids between the inner and outer leaflets. To better understand these dynamics, we prepared model bilayers by sequential deposition of monolayers composed of either a single lipid component, or a mixture of lipids and cholesterol, using the Langmuir Blodgett/Langmuir Schaeffer (LB/LS) method. These solid supported bilayers were investigated by the interface-specific vibrational sum frequency generation (VSFG) spectroscopy, which is uniquely sensitive and selective to the chemical composition and asymmetry of the bilayer. Preliminary measurements showed that mixtures containing DOPC and POPC, together with DSPC and cholesterol, yield appreciable SFG signals even for symmetrically formed bilayers. This was attributed to the presence of coexisting ordered and disordered phase domains, consistent with observations in freely floating vesicles of the same composition. Interestingly, the SFG signal of symmetric bilayers persisted even upon heating the sample above the miscibility transition temperature T_{misc} , an indication that either (1) significant lipid clustering persists even above T_{misc} , or (2) there is an inherent bilayer asymmetry due to interactions with the quartz substrate. VSFG alone cannot distinguish between these two scenarios, and therefore neutron reflectometry (NR) combined with selective lipid deuteration was used to quantify the chemical composition and thicknesses of the leaflets. Together, the NR and VSFG techniques allowed us to quantify translocation kinetics, and to better understand the preferential migration of lipids in a complex bilayer system above and below the phase transition temperature.

COLL 665

Peptide-grafted gold nanoparticles studied with ReaxFF MD simulations

Tao Wei, tao.wei@howard.edu. Lamar University, Beaumont, Texas, United States

Gold nanoparticles (NPs) chemically modified with peptides have important applications in drug delivery. The nature and strength of NP-peptides interactions affect the properties of NPs. Their interactions consist of nonbonding (Lenard-Jones and electrostatics) and weak covalent bonding, such as thiol-Au. Moreover, amino acid residues of peptides can display various protonation states at the NP interface due to the local complex interactions around NP surfaces and the difference of local ion concentration, water concentration and pH compared to the bulk environment. In this study, Reactive forcefield (ReaxFF) molecular dynamics (MD) simulations were

performed to study both physical and chemical properties of peptide-grafted Au NPs. The different factors, including surface packing density, types of peptides, and grafted chain length have been systematic studied. Our studies with ReaxFF MD simulations will provide better understanding of Au NPs' properties by incorporating chemical reactions.

COLL 666

Bovine serum albumin protein surface properties in the presence of polymers or surfactants

Amir Erfani¹, aerfani@okstate.edu, Shahin Khosharay², Nicholas H. Flynn¹, Josh D. Ramsey¹, Clint Aichele¹. (1) Chemical Engineering, Oklahoma State Univeristy, Stillwater, Oklahoma, United States (2) Iranian Institute of Research & Development in Chemical Industries, Tehran, Iran (the Islamic Republic of)

Proteins are among the macromolecules that are now being extensively studied for possible therapeutic purposes. For most applications, the therapeutic proteins are accompanied or encapsulated in surfactants or polymers which act as engineered vehicles for drug delivery applications. The aim of this work is to investigate how a model protein interacts with drug delivery enhancers, including either surfactants or polymers. One way to determine these interactions is to measure surface tension and develop a model to predict the interactions. To achieve this aim, the surface properties of aqueous systems of Bovine Serum Albumin (BSA), polylysine, polyethylene glycol and two different surfactants are studied. The pendant drop method is used to measure the static and dynamic surface tensions. Dynamic surface tension is used to indicate the rate of the interfacial adsorption of the protein. Furthermore, the equilibrium surface tensions can show the overall driving force of the protein to migrate to the surfaces and the interaction between the protein and the surfactant/polymer. The equilibrium surface tensions are modelled by the equality of surface and bulk chemical potentials of the components. The molar surface area and surface to solution distributions for each aqueous solution of protein, polymer, and surfactant are obtained. These parameters are utilized to predict the surface properties of protein-polymer and protein-surfactant systems. Furthermore, the dynamic surface tensions for these systems are modeled using non-equilibrium thermodynamics and the chemical affinity model. This model is used to quantify the kinetic parameters of the interfacial adsorption. Results of this study will help researchers design better micro or nanoparticles that can carry therapeutic proteins.

COLL 667

Adsorption orientation of amyloidogenic peptides over nano-gold colloidal particles' surfaces

Kazushige Yokoyama, yokoyama@geneseo.edu. Chemistry, The State University of New York Geneseo College, Rochester, New York, United States

The adsorption of amyloidogenic peptides; amyloid beta 1-40 (Ab₁₋₄₀), alpha-synuclein (a-syn), and beta 2 microglobulin (b2M) were attempted over nano-gold colloidal particle's surface. The spectroscopic inspection extracted the critical pH point (pH_o) at where the color change of the amyloidogenic peptide coated nano-gold colloids occurrence of an aggregation of nano-gold colloid particles. The change of surface property caused by a degree of coverage of peptides reflected upon the DpH_o, which is a difference of pH_o between that of a bare gold nano colloid and that of peptide coated gold colloid. We extracted the q (peptide coverage ratio) for all amyloidogenic peptides over gold colloid of different sizes. The geometric analysis and simulation concluded that spiking out prolate shaped peptides cross each other with a skewed angle over nano interface. While more spherical shape of a peptide was required for the lower q. This "spiked-out" orientation strongly suggests that contacting spot for Ab₁₋₄₀ to be Lysine at 23rd sequence (²³K⁺) structure and rough number of adsorbed amyloidogenic peptides on each gold colloidal surface.

COLL 668

Ionic strength-mediated phase transitions of surface-adsorbed DNA on single-walled carbon nanotubes

Daniel Salem¹, dpsalem@mit.edu, Xun Gong¹, Albert Tianxiang Liu³, Volodymyr Koman⁴, Juyao Dong⁵, Michael Strano². (1) Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Chemical Engineering, 66-566, MIT, Cambridge, Massachusetts, United States (3) Massachusetts Institute of Technology, Cambridge, MA, Massachusetts, United States (5) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Single-stranded DNA oligonucleotides have unique, and in some cases sequence-specific molecular interactions with the surface of carbon nanotubes that remain the subject of fundamental study. In this work, we observe and analyze a generic, ionic strength-mediated phase transition exhibited by over 25 distinct oligonucleotides adsorbed to single-walled carbon nanotubes (SWCNTs) in colloidal suspension. The phase transition occurs as monovalent salts are used to modify the ionic strength from 500 mM to 1 mM, causing a reversible reduction in the fluorescence quantum yield by as much as 90%. The phase transition is only observable by fluorescence quenching within a window of pH and in the presence of dissolved O₂, but occurs independently of this optical quenching. The negatively charged phosphate backbone increases (decreases) the DNA surface coverage on an areal basis at high (low) ionic strength, and is well described by a two-state equilibrium model. The resulting quantitative model is able to describe and link, for the first time, the observed changes in optical properties of DNA-wrapped SWCNTs with ionic strength, pH, adsorbed O₂, and ascorbic acid. Cytosine nucleobases are shown to alter the adhesion of the DNA to SWCNTs through direct protonation from solution, decreasing the driving force for this phase transition. We show that the phase transition also changes the observed SWCNT corona phase, modulating the recognition of riboflavin. These results provide insight into the unique

molecular interactions between DNA and the SWCNT surface, and have implications for molecular sensing, assembly, and nanoparticle separations.

COLL 669

Flavin self-assemblies towards chiral enrichment of single-walled carbon nanotubes

Erandika Karunaratne^{1,2}, erandika.karunaratne@uconn.edu, Mehdi Mollahosseini^{1,2}, Fotios Papadimitrakopoulos^{1,2}. (1) Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States

Single-wall carbon nanotubes (SWNTs) have attracted great interest for various applications due to their unique mechanical, electrical, optical, and chemical properties. However, separation of SWNTs into populations of single-chirality, which is required in electronic and optical applications, remains challenging. Recent studies have shown that the organization of special surfactants around single-walled carbon nanotubes allows selective extraction of SWNTs. Our group has shown that flavin mononucleotide (FMN) and its aliphatic (dodecyl) analog FC12 self-organize in a helical pattern around SWNTs while enriching (8,6) chirality. Understanding of molecular motifs and relative interactions behind this selective self-assembly may allow us to develop a strategy that can be used to select any chirality. To this effect, we investigated X-Ray diffraction of the FMN crystals nucleated from (8,6)-enriched nanotubes. Moreover, self-assemblies of FC12 and a smaller analog of FC12, *i.e.* lumazine (LC10) around different (*n,m*)-SWNTs were studied using spectroscopy and molecular mechanics calculations. The aim of this study is to elucidate the organizational pattern of different flavin derivatives around SWNTs, which can reveal the underlying recognition pattern leads to chiral selectivity.

COLL 670

Effects of β -sitosteryl sulfate on the phase behavior and hydration properties of phospholipids

Hideki Sakai¹, hisakai@rs.noda.tus.ac.jp, Kafle Ananda¹, Masaaki Akamatsu¹, Kenichi Sakai¹, Chihiro Kaise², Teruhisa Kaneko². (1) Faculty of Science and Technology, Tokyo University of Science, Chiba, Japan (2) L.V.M.C. Inc., Tokyo, Japan

Phosphatidylcholines (PCs) are amphipathic molecules, which constitute the building block of biological membranes. They form various biologically and industrially important mesophases. Fully saturated phospholipids like DPPC and DSPC mainly exhibit three types of phases depending on temperature, namely, the gel phase ($L\beta'$), ripple ($P\beta'$) phase, and liquid crystalline ($L\alpha$) phase. Sterols such as cholesterol, β -sitosterol, cholesterol sulfate, etc. tend to fluidize these membranes, hence giving rise to new phases. Studies conducted so far in this field are focused mainly on the PC membranes

containing –OH sterols (cholesterol, β -sitosterol, stigmasterol, etc.). Sterol sulfates are found to possess antibacterial potentials. Phytosteryl sulfates possess one more advantage of being derived from plant sources and causing less impact on health and environment. However, despite their merits, no attempt seems to have been made on studying the membranes consisting of phytosteryl sulfates. Therefore, to fulfill this need, we are studying the effects of sodium beta-sitosteryl sulfate on the phase behavior and hydration properties of pure and mixed phosphatidylcholines.

Multilamellar stacks were prepared from the PCs as well as PC-PSO₄ mixtures by solvent evaporation followed by hydration. They were then studied using SWAXS, DSC, and microscopy.

Polarizing optical microscopy (POM) textures gradually change into “oily streaks”, from the initial “maltese crosses”, or “white birefringence”. In the case of DPPC, both, the DSC thermograms as well as WAXS peaks are eliminated with the mole fraction (x) of PSO₄ ≥ 0.3 , whereas, in the case of DSPC, they are not fully eliminated. It implies that, in the case of DPPC, PSO₄ completely fluidizes the membrane, whereas, in the case of DSPC, it only partly does so. Further, the DSC, SAXS and POM data suggest an enhanced hydration of the membranes with the addition of PSO₄. The enhanced membrane hydration in this way, as well as its fluidization, can find applications in cosmetics and pharmaceutical formulations.

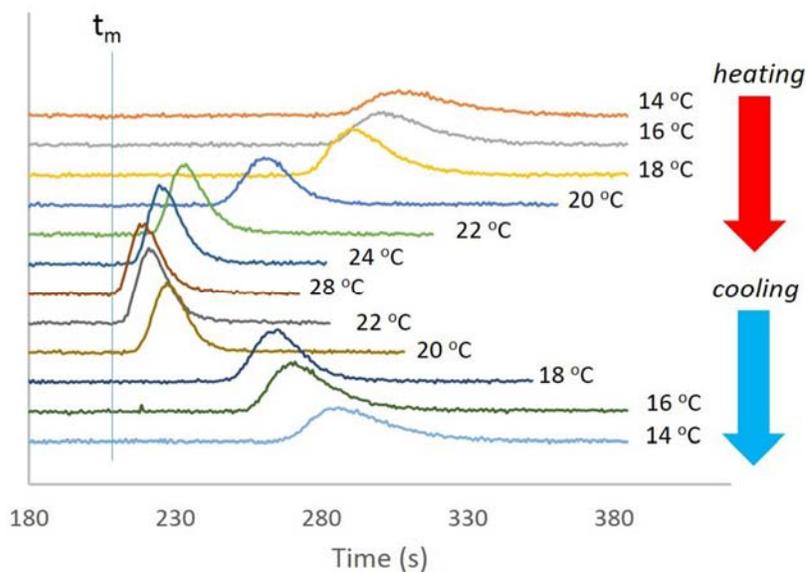
COLL 671

Direct measurement of metal ion binding to ionophores in lipid bilayers by affinity chromatography

Eric E. Ross, rosse@gonzaga.edu. Gonzaga University, Spokane, Washington, United States

Metal:ionophore complex formation is part of the mechanism for ion selectivity and translocation by carriers and by many channels. The measurement of apparent binding constants for ion:ionophore complexes within lipid membranes is difficult because the interactions are generally weak and lipid bilayer structures can impose constraints on the use of many analysis techniques. There is not an abundance of experimental binding data for otherwise well-characterized ionophores such as valinomycin and gramicidin. We report the development of a micro-scale affinity chromatography method based on silica colloid-supported lipid bilayers and describe the characterization of group I ion binding to carrier ionophores valinomycin and nigericin, and to the channel-former gramicidin within different lipid stationary phases. Ion binding to carrier ionophores are sensitive to lipid phase whereas binding to the channel-former gramicidin is not. Unexpectedly, the observed binding behavior of valinomycin is substantially different in the gel phase of DMPC versus DPPC lipids. Cationic complexes are stabilized by anionic lipids in the bilayer. Mobile phase components that block or compete with ionophore binding reduce group I ion retention times. Split peaks observed for potassium and rubidium ions interacting with gramicidin appear to arise from competitive interactions at a single binding site; monovalent competitors remove the split peak behavior whereas divalent metals that block the channel do not. In total,

the observations of binding behavior both predicted and unexpected with diverse formulations of lipid bilayers indicate the potential of this technique to complement other methods for the study of ion:ionophore complexation.



Chromatographic retention of K⁺ on valinomycin-containing DMPC supported bilayers.

COLL 672

Entropy-driven self-assembly of protein 2D liquid crystal at solid-liquid interface

Shuai Zhang¹, *inanoshuai@gmail.com*, **Harley Pyles**², **David Baker**², **Jim J. DeYoreo**¹. (1) *Pacific Northwest National Laboratory, Richland, Washington, United States* (2) *University of Washington, Seattle, Washington, United States*

Self-assembly at solid-liquid interface is a promising way to synthesize hierarchical protein functional architectures in nature. For instance, collagen can self-assemble into matrix for biomineralization and bone growth; and membrane proteins can form channels on cell-membrane to transport ions, small molecules and macromolecules. In another example, S-layer protein self-assembles on cell envelop of bacteria to mechanically and osmotically stabilize bacterial cells. To mimic those protein structures and functions, and to inspire the design of novel protein functional materials, understanding the rules to control protein kinetic and thermodynamic behaviors is necessary.

In this work, we used in-situ high-resolution and high-speed atomic force microscopy (AFM) to study the dynamic behaviors and self-assembly structures of protein nanorod at mineral-liquid interface in electrolyte. By tuning the hydration force between protein nanorods, and between protein and interface, we are able to achieve protein 2D liquid crystal with millimeter-rang order. After tuning the aspect ratio of the protein nanorods, introducing end-end hydrophobic interaction between the nanorods, we prove the formation of protein 2D liquid crystal can be described by the model of entropy-driven

self-assembly of colloidal nanocrystals. Using the obtained knowledge, we further synthesize well-ordered hexagonal protein network at solid-liquid interface. That is considered as a big step to artificially control protein 2D architectures with higher order of complexity.

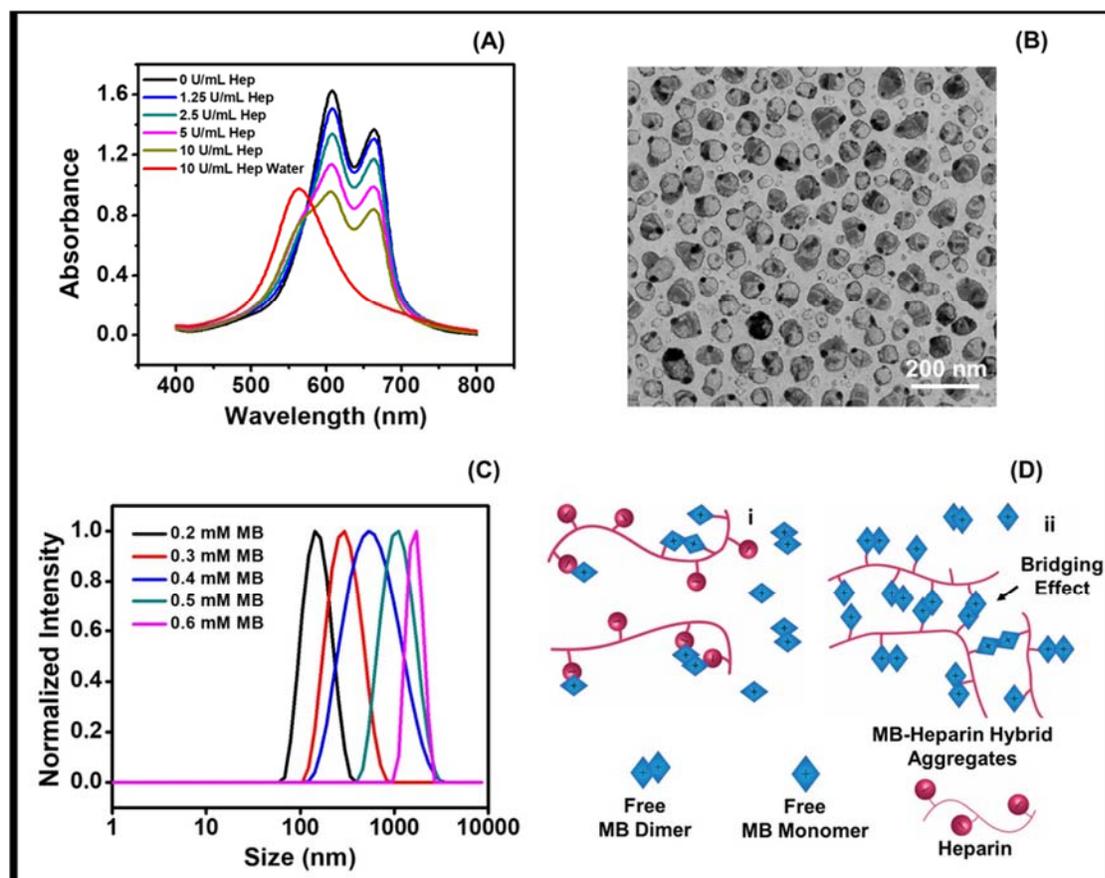
We believe that this work is helpful to summarize the general model to describe surface assisted self-assembly of hierarchical biomaterials. It also inspires strategies to create artificial bio-mimetic materials with various applications.

COLL 673

Mechanistic investigation of methylene blue and heparin interaction in phosphate buffer saline

Junxin Wang¹, junxinud@gmail.com, Kathryn Humphries², Bill Miller², Jesse V. Jokerst¹. (1) University of California San Diego, La Jolla, California, United States (2) Truman State University, Kirksville, Missouri, United States

Methylene blue (MB) is FDA-approved and the interaction with the important anticoagulant heparin has been investigated spectroscopically in water. However, details of the interaction in physiological conditions remain unclear. Here, we provide a mechanistic investigation to study the binding kinetics between MB and heparin in phosphate buffer saline (PBS). We noted a 0.04 ppm chemical shift of the proton in the phenothiazine ring of MB in the nuclear magnetic resonance spectrum suggesting electron delocalization and self-aggregation of MB. The absorbance peak of 0.15 mM MB blue shift from 680 to 610 nm upon addition of heparin, even at a high heparin concentration (i.e. 10 U/mL) (**Panel A**). This indicated that MB formed dimers rather than higher order aggregates as in water. This is because sodium chloride causes dissociation. In addition to MB self-aggregation, we also observed nanoscale MB-heparin hybrid aggregates in transmission electron microscope (TEM) (**Panel B**). The dynamic light scattering (DLS) analysis showed that the aggregate size (100 nm-2 μ m) was governed by MB concentration rather than the heparin (**Panel C**). We attributed the formation of aggregates to the bridging effect of MB that connected two heparin chains sufficiently bound with MB (**Panel D**). To verify our hypothesis, we used molecular dynamics simulations to analyze the binding energy, the energy decomposition, and the MB concentration dependent binding activity of MB and heparin.



Panel A shows the absorbance spectra of MB upon additions of heparin in PBS and water. TEM images reveal MB-heparin hybridized aggregates in the corresponding samples (panel B). Panel C indicates that the aggregates size was a function of MB concentration. The underlying mechanism was illustrated in panel D.

COLL 674

Dendritic effect and magnetic permeability in dendronized magnetic nanoparticles

Jennifer D. Lee², jleed@sas.upenn.edu, **Davit Jishkariani**^{1,6}, **Hongseok Yun**¹, **Taejong Paik**³, **James M. Kikkawa**⁴, **Cherie R. Kagan**^{5,1}, **Bertrand Donnio**^{6,7}, **Christopher B. Murray**^{1,8}. (2) Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States (3) University of Pennsylvania, Philadelphia, Pennsylvania, United States (4) Physics, University of Pennsylvania, Philadelphia, Pennsylvania, United States (5) Dept of ESE MSE, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States (6) Complex Assemblies of Soft Matter Laboratory (COMPASS), CNRS-Solvay-University of Pennsylvania, Bristol, Pennsylvania, United States (7) Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS–Université de Strasbourg, Strasbourg, France (8) Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

To miniaturize AC magnetic devices, it is imperative to consider the ferromagnetic resonance (FMR) frequencies as this often limits the operable frequency range. The tunability of dipole-dipole interactions can be utilized to increase the FMR limit to a higher frequency range (i.e. radio frequency). Colloidal magnetic nanoparticles (NPs) have been widely used in the design of inductors and transformers to reduce the volume of magnetic components. In this contribution, we fine tune the inter-particle spacings with the use of dendritic coatings on colloidal magnetic NPs. A series of dendritic ligands with various end-groups was designed to bind to the NPs *via* ligand exchange. The structure of dendrons is based on 2,2-bis(hydroxymethyl)propionic acid with one NP binding group and several fatty acid end-groups per each ligand. Using Ni NPs capped with dendritic ligands of increasing generations (G0 to G3), the inter-particle spacing was varied from 2.9 to 5.0 nm. We achieved the control of inter-particle spacings and identified the generation with the most optimal geometry. These insights will be useful for predicting future ligand architectures. Using G2, the dendron with highest inter-particle separation per molecular weight, the effect of inter-particle dipole-dipole interactions altered the magnetic properties of NPs without sacrificing the colloidal properties and solution processability. The effect of changing dipole-dipole interactions was correlated with the direct current and alternating current magnetic properties of manganese zinc ferrite (MZF) NPs, and particularly, the FMR frequency of the MZF NPs increases from 234 MHz to over 500 MHz, suggesting the potential of this approach to increase the FMR limit to higher frequency ranges.

COLL 675

Ligand-mediated near-infrared photoluminescence of small diameter copper, silver, and gold nanoparticles

Scott Crawford, sec66@pitt.edu, Christopher M. Andolina, Ashley Smith, Kathryn Johnston, Lauren Marbella, Patrick Straney, Jill Millstone. Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

Small gold nanoparticles (~1.4–2.2 nm core diameters) exist at an exciting interface between molecular and metallic electronic structures. These particles have the potential to elucidate fundamental physical principles driving nanoscale phenomena and to be useful in a wide range of applications. Here, we study the optoelectronic properties of aqueous, phosphine-terminated gold nanoparticles (core diameter = 1.7 ± 0.4 nm) after ligand exchange with a variety of sulfur-containing molecules. No emission is observed from these particles prior to ligand exchange, however the introduction of sulfur-containing ligands initiates photoluminescence. Further, small changes in sulfur substituents produce significant changes in nanoparticle photoluminescence features including quantum yield, which ranges from 0.13 to 3.65% depending on substituent. Interestingly, smaller ligands produce the most intense, highest energy, narrowest, and longest-lived emissions. Radiative lifetime measurements for these gold nanoparticle conjugates range from 59 to 2590 μ s, indicating that even minor changes to the ligand substituent fundamentally alter the electronic properties of the luminophore itself. These results isolate the critical role of surface chemistry in the photoluminescence of small

metal nanoparticles and largely rule out other mechanisms such as discrete (Au(I)—S—R)_n impurities, differences in ligand densities, and/or core diameters. The results from these experiments are then applied to the less noble coinage metals (e.g. silver and copper) which share the same valence electronic configuration as gold. We then demonstrate that copper and silver nanoparticles of analogous size, shape, and surface chemistries as gold nanoparticles exhibit comparable luminescent properties, a critical step in the design of cost-effective luminescent particles.

COLL 676

NHC-capped polymers for surface functionalization of metal nanoparticles in aqueous solution

Srinivas Thanneeru¹, *savin1986@gmail.com*, **Kaitlynn Ayers**¹, **Murali Anuganti**¹, **Lei Jin**¹, **Lei Zhang**¹, **Gael Ung**¹, **Jie He**^{1,2}. (1) Dept of Chemistry, University of Connecticut, Storrs, Connecticut, United States (2) Polymer Program, Institute of Material Science, University of Connecticut, Storrs, Connecticut, United States

In solution, nanoparticles (NPs) are normally stabilized with surface ligands, such as thiols, phosphines, and amines. These ligands are unstable in presence of oxygen saturated aqueous and oxygen-rich biological media. N-heterocyclic carbenes (NHCs), on the other hand, are excellent ligands that bind to a variety of metal ions with extremely high binding strength via σ donation. NHCs as ligands are stable under oxygen-rich conditions. However, there are only a few studies of NHC ligands for metal NPs in literature, largely due to synthetic challenges of carbene. In particular their sensitivity as free NHCs to oxygen and water largely limits the application of NHC ligands for metal NPs. We report a general method to prepare NHC-functionalized polymers to modify metal NPs in water using a facile transmetallation. NHC-functionalized polymers can be prepared using simple post-polymerization functionalization of polymers capped with halogen atoms (e.g., Cl and Br) synthesized via atom transfer radical polymerization (ATRP). When reacted with N-methyl imidazole, halogen-ended polymers can be converted to yield imidazolium salt and further transferred into Cu(I)-NHC-capped polymers in presence of a weak base, e.g., K₂CO₃ and Cu(I)Cl. Cu(I)-NHC-capped polymers are stable in water and can be used to modify metal NPs using transmetallation in any good solvents of polymers. The surface modification of citrate-capped gold NPs has been examined using a ligand exchange method in an emulsion solution. The NHC polymer-capped gold NPs are able to disperse in a series of organic solvents based on the solubility of polymer ligands. We show the successful surface modification of gold NPs using both hydrophobic and hydrophilic polymers, including polystyrene, poly(methyl methacrylate), poly(*n*-butyl acrylate) and poly(2-(2-methoxyethoxy)ethyl methacrylate) functionalized with carbenes. The stability of NHC capped AuNPs in various conditions such as high salt concentrations (1M NaCl) and hydrophobic solvents has been examined. This method will open the doors to use the carbene functionalized polymers for the surface modification of other metal or metal oxide NPs for potential applications in nanomedicine and nanocatalysis.

COLL 677

Surface modification of carbon-based material with terminal alkene ligands using radical coupling reactions

Yongqian Zhang¹, *kelly_lilac@hotmail.com*, **Robert J. Hamers**². (1) Chemistry, University of Wisconsin- Madison, Madison, Wisconsin, United States (2) Univ of Wisconsin, Madison, Wisconsin, United States

Functionalized nanoparticles have been reported to have enhanced biological response compared with non-functionalized nanoparticles, but the response can vary significantly depending on the nanoparticle composition and the molecular structure of the surface molecular layers. Diamond nanoparticle provides an ultra-stable platform for investigating how surface properties influence nanoparticle behavior and therefore is an ideal material for mechanistic studies of nanoparticle aggregation and toxicity. However, to come to fruition it is necessary to develop *more scalable, robust, benign, and selective* method of functionalizing diamond nanoparticle. In our previous work, we have used photochemical grafting methods to modified diamond nanomaterials; but these methods are not readily applied to many applications due to the inefficient nature of the photochemical grafting mechanism. Recently, we have developed a novel surface functionalization method using radical chemistry to attach alkene terminal ligands to diamond nanoparticle surface.

In this talk we will explore attaching various alkene terminal ligands (both hydrophobic and hydrophilic) on diamond nanoparticle surface, as well as other carbon-based materials. We will demonstrate details on how these ligands bind to the nanoparticle surfaces, and provide characterization of the corresponding surface/ligand structures after functionalization using X-ray photoelectron spectroscopy and high-resolution (liquid phase) NMR.

COLL 678

Chiro-magnetic nanoparticles and gels

Jihyeon Yeom¹, *jyeom@umich.edu*, **Uallisson Santos**², **Mahshid Chekini**¹, **Minjeong Cha**¹, **André de Moura**², **Nicholas Kotov**¹. (1) University of Michigan, Ypsilanti, Michigan, United States (2) Federal University of São Carlos, São Carlos, Brazil

Chiral inorganic nanostructures have high circular dichroism, but real-time control of their optical activity has so far been achieved only by irreversible chemical changes. Field modulation is a far more desirable path to chiroptical devices. We hypothesized that magnetic field modulation can be attained for chiral nanostructures with large contributions of the magnetic transition dipole moments to polarization rotation. We found that dispersions and gels of paramagnetic Co₃O₄ nanoparticles with chiral distortions of the crystal lattices exhibited chiroptical activity in the visible range that was 10 times as strong as that of nonparamagnetic nanoparticles of comparable size.

Transparency of the nanoparticle gels to circularly polarized light beams in the ultraviolet range was reversibly modulated by magnetic fields. These phenomena were also observed for other nanoscale metal oxides with lattice distortions from imprinted amino acids and other chiral ligands. The large family of chiral ceramic nanostructures and gels can be pivotal for new technologies and knowledge at the nexus of chirality and magnetism.

COLL 679

Setting carriers free – healing faulty interfaces promotes delocalization and transport in nanocrystal solids

Willem Walravens¹, willem.walravens@ugent.be, Nayyera Mahmoud^{2,1}, Filip Geenen⁶, Eduardo Solano³, Jolien Dendooven⁶, Athmane Tadjine⁵, Christophe Delerue⁵, Gunther Roelkens², Christophe Detavernier⁶, Zeger Hens⁴. (1) Department of Chemistry, Ghent University, Ghent, Belgium (2) Photonics Research Group, Ghent University, Ghent, Belgium (3) ALBA Synchrotron Light Source, Cerdanyola del Vallès, Spain (4) Ghent University, Ghent, Belgium (5) Department ISEN, IEMN, Lille Cedex, France (6) Conformal Coating of Nanomaterials, Ghent University, Ghent, Belgium

Nanocrystal building blocks can be assembled to make an artificial, nanocrystal solid. The choice of building block and the way they are assembled set up pathways to make new and unique materials with tailored properties. A case in point are superlattices of semiconductor nanocrystals or quantum dots (QDs), which find applications in, e.g., photodetectors, solar cells and field-effect transistors. Quantum dots offer the appealing combination of a tunable band gap, a high absorption coefficients, and a suitability for solution-based processing. QD films are typically produced through, e.g., spincoating, dropcasting or spraycoating. This results in disordered nanocrystal stacks, where poor electronic transport can be caused by excessive surface defects or restricted dot-to-dot hopping. To disentangle such effects, we analyzed the delocalization and transport of charge carriers in 2D superlattices of epitaxially connected QDs. In the case of PbS and PbSe QDs, such superlattices can be formed over several square micrometer. Using elemental analysis and structural analysis by in-situ XRF and GISAXS, respectively, we show that such lattices keep their structural integrity in a wide temperature window, ranging up to 320 °C and more; an ideal starting point to assess the effect of gentle thermal annealing on the superlattice properties. We find that annealing such superlattices at temperatures ranging from 75-150 °C induces a marked redshift of the QD band-edge transition. In fact, the band-edge found after annealing agrees, opposite from state-of-the-art literature, with theoretical predictions on charge carrier delocalization in such epitaxially connected superlattices. In addition, we observe a 1000-fold increases of the charge carrier mobility after mild annealing. While the superstructure remains intact at these temperatures, an XRD rocking curve analysis indicates that annealing markedly decreases the density of grain boundaries. This indicates that the presumably epitaxial connections between QDs in as-synthesized superlattices still form a major source of grain boundaries and defects, to an extend that

carrier delocalization over multiple QDs is prevented and dot-to-dot transport remains strongly restricted.

COLL 680

Wavefunction engineering in CdSe/PbS core/shell heterostructures

Brian M. Wieliczka^{1,2}, brianwieliczka@wustl.edu, **William E. Buhro**^{1,2}, **Richard A. Loomis**^{1,2}. (1) Chemistry, Washington University in St. Louis, St. Louis, Missouri, United States (2) Institute for Materials Science and Engineering, Washington University in St. Louis, St. Louis, Missouri, United States

The synthesis and optical characterization of CdSe/PbS quantum dots (QDs) is reported. The spectroscopic behavior of these particles demonstrates their potential for use in optoelectronic devices, taking advantage of wave function engineering of the electron and hole. With increasing shell thickness, the band edge absorption and photoluminescence transitions decrease in energy as a result of reduced quantum confinement. At the same time, the first absorption transition strength decreases by over an order of magnitude relative to the higher energy transitions due to reduced electron—hole wavefunction overlap in the core/shell QDs, leading to a tunable shift between the onset of strong absorption and photoluminescence of up to 550 meV. These changes in wavefunction overlap are further corroborated by effective mass approximation wavefunction calculations, which show a transition between quasi-type-I and quasi-type-II behavior. These results demonstrate the prospects for this system as luminescence solar concentrators with a tunable emission energy.

COLL 681

Colloidal synthesis and photophysical characterization of SiGeSn alloy quantum dots

Ebtesam Eladgham^{1,2}, eladghameh@vcu.edu, **Umit Ozgur**³, **Denis O. Demchenko**⁴, **Indika U. Arachchige**⁵. (1) Chemistry, Virginia Commonwealth University, Richmond, Virginia, United States (2) Solar Energy, National Research Centre, Giza, Egypt (3) Electrical and Computer Engineering, Virginia Commonwealth University, Richmond, Virginia, United States (4) Physics, Virginia Commonwealth University, Richmond, Virginia, United States (5) Chemistry, Virginia Commonwealth University, Henrico, Virginia, United States

Si and Ge have gained significant interest in optoelectronic and energy-related technologies. Alloying them together has been shown to increase the light-matter interactions, widening the absorption and emission spectrum. The real problem with this system is the inherent indirect energy gaps that significantly limit the efficiency of optical transitions. Incorporation of Sn has been shown to induce an indirect-to-direct band structure crossover resulting in high optical efficiencies. Recently, nanoscale alloying of Ge and Sn has been elucidated to produce GeSn quantum dots that exhibit size- and

composition-tunable direct and indirect energy gaps in the visible to near IR spectral region. However, neither the SiGe nanoalloys nor the ternary SiGeSn nanoalloys are reported by wet chemical syntheses. Herein, we report the first colloidal synthesis of ternary SiGeSn alloy quantum dots with tunable energy gaps and bright yellowish to orange color emission properties. The effect of synthetic parameters on the primary particle size, morphology, composition, fundamental band structure, and optoelectronic properties will be discussed.

COLL 682

Synthesis of quaternary Cu-Zn-In-S nanocrystals and photovoltaic characteristics

Ruwini D. Rajapaksha, *ruwini.rajapaksha@student.nmt.edu*, Mahinda I. Ranasinghe. *Chemistry, New Mexico Institute of Mining and Technology, Socorro, New Mexico, United States*

Highly luminescent Quaternary Cu-Zn-In-S (CZIS) nanocrystals (NCs) were synthesized via direct hot injection method. The low toxic chloride metal precursors and non-coordinate, high boiling solvent 1-Octadecene were employed for this synthesis. The optical properties of synthesized NCs were tuned by changing the composition of metal precursor ratios. Two sets of composition of metal precursor ratios were studied by changing the Cu: Zn metal precursor ratio and the Cu: In metal precursor ratio. The synthesized NCs shows the tunable photoluminescence (PL) spectra of emission color from NIR to visible region with the variation of metal precursor ratios. The synthesized NCs shows narrow size distribution and average size of 2.5 - 4 nm. The time-resolved fluorescence decay studies and time-correlated single photon counting spectroscopic studies were carried out to study the photophysical dynamics and fluorescence (FL) lifetime of these quaternary NCs. The synthesized NCs shows tunability of FL lifetime with the variation of composition of the metal precursor's ratios and shows the longer FL lifetimes. These type of quaternary NCs shows promising applications in solar cells, light emitting diodes and biological imaging studies. To investigate the use of this synthesized NCs in solar cell applications the quantum dot sensitized solar cells (QDSSC) were fabricated and their photovoltaic characteristics were studied with the different metal precursor's compositions.

COLL 683

Kinetically controlled aggregation and growth, a pathway for synthesis simple-branched to hyperbranched NCs

Mohammad Sadegh Yazdanparast, *yazdanparast@ksu.edu*. *Chemistry, Kansas State University, Manhattan, Kansas, United States*

Nanocrystals with different composition and morphologies have attracted a lot of attention due to their applications in different devices such as photovoltaic, photoelectrochemical and photoelectronic devices. Branched semiconductor

nanocrystals have large surface-area which makes them better candidates for photovoltaic cells. CdS_{1-x}Se_x nanocrystals are synthesized in a reaction of a mixture of dichalcogenides with cadmium precursor using microwave assistance. By controlling the ratio of dichalcogenides, the composition of NCs can be tuned. The shape of resulted nanocrystals changes from spherical to simple branched and hyperbranched. The study shows the NCs are being formed in three steps of nucleation, aggregation, and growth. By controlling each step the morphology of final NCs can be controlled.

COLL 684

Autonomous thermal-oxidative composition inversion (TOCI) and texture tuning in liquid metal particles

*Joel Cutinho¹, Boyce S. Chang¹, Ian D. Tevis², **Martin M. Thuo¹**, mwangi.m@gmail.com. (1) Materials Science & Engineering, Iowa State University, Ames, Iowa, United States (2) Safi-Tech inc, Ames, Iowa, United States*

Droplets capture an environment-dictated equilibrium state of a liquid material. Equilibrium, however, often necessitates nanoscale interface organization especially where passivating layers form. Herein, we demonstrate that this kinetic-driven organization may predispose a material to autonomous thermal-oxidative composition inversion (TOCI) and texture reconfiguration under felicitous choice of trigger. We exploit inherent structural complexity, differential reactivity, and metastability of the ultra-thin (~0.7-3 nm) passivating oxide layer on eutectic gallium-indium (EGaIn, 75.5 % Ga, 24.5% In w/w) core-shell particles to illustrate this new approach to surface engineering. Two tiers of texture can be produced on thermal processing with the first evolution showing crumpling while the second is a particulate growth above the first uniform texture. This process leads to inversion in composition of the surface oxide, with higher indium content on the surface in lieu of gallium. Controlled thermal treatment of liquid EGaIn, therefore leads to tunable surface roughness and composition inversion. We infer that this tunability is due to structure of the passivating oxide layer that is driven by differences in reactivity of Ga and In, and requisite enrichment of the less reactive component at the metal-oxide interface.

COLL 685

MnO₂ and MoS₂ nano-knives exhibit antibacterial properties

*Farbod Alimohammadi¹, **Mohammad Sharifian Gh.¹**, tue84271@temple.edu, Nuwan H. Attanayake², Akila Thenuwara³, Yury Gogotsi⁴, Babak Anasori⁵, Daniel R. Strongin⁶. (1) Department of Chemistry, Temple University, Philadelphia, Pennsylvania, United States (4) Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States*

Two-dimensional nanomaterials (also known as nanosheets) have attracted considerable attention in biomedical and environmental applications due to their

antimicrobial properties. In the present research we investigated the role of 'nano-knife' characteristics of nanosheets for their antibacterial properties. Toward this end, antibacterial properties of MnO₂ and MoS₂ (supported on graphene oxide or Ti₃C₂T_x MXene) were investigated toward Gram-positive and Gram-negative bacteria. *Bacillus subtilis* and *Escherichia coli* bacteria were chosen as the model organisms and were treated individually with 100 µg/mL of the randomly oriented and vertically aligned nanosheets for ~3 h in the dark. The viability measurements of bacteria, performed by flow cytometry and fluorescence imaging, showed that vertically aligned MnO₂ and MoS₂ nanosheets exhibited the highest antimicrobial activity in which Gram-positive bacteria showed a higher loss in membrane integrity. Moreover, scanning electron microscopy images suggested that the nanosheets compromised the cell wall upon interaction which led to significant bacterial morphological changes. We propose that the peptidoglycan mesh in the bacterial wall is likely the primary target of the nanomaterials.

COLL 686

Time-gated fluorescence imaging and sensing using long lifetime near infrared quantum dots

*Manon Debayle, Nicolas Lequeux, Vincent Loriette, alexandra Fragola, **Thomas Pons**, thomas.pons@espci.fr. LPEM, ESPCI, Paris, France*

In vivo fluorescence imaging is widely used to probe biological phenomena in whole live organisms, thanks to its low cost, flexibility and noninvasiveness. The sensitivity of fluorescence imaging is however limited by (i) absorption and diffusion of light by tissues, which limit photon detection as the imaging depth increases and (ii) autofluorescence from intrinsic fluorophores, which causes an important inhomogeneous background signal. The former issue can be addressed by the use of emitters that can be excited and re-emit in the near infrared range to reduce light scattering and absorption. The latter can be addressed either by the use of upconversion probes or by time-gated fluorescence imaging (TG-FI). TG-FI uses a controllable delay between a pulsed excitation and fluorescence emission detection. This enables collecting photons from longer lifetime probes and rejecting those from shorter lifetime intrinsic fluorophores, which have a typical decay time of a few ns.

Here we present the use of near infrared emitting CuInSe₂-based, quantum dots (QDs) for TG fluorescence imaging and sensing. These probes both emit and are excitable in the NIR range, which optimizes the imaging depth in live specimen. Their typical decay time is on the order of 150-300 ns, which lies in the ideal range for TG-FI. In a first application, ZnCuInSe/ZnS QDs with optimized optical properties were coated with a multidentate imidazole-zwitterionic block copolymer and incorporated into live lymphoma cells. This surface chemistry enables long term (=several days) stability in the cytoplasm of live cells without aggregation or loss of optical properties. These cells were then injected intravenously in a rat model. We show that QD-based TG-FI enables a complete elimination of the autofluorescence background and strongly enhances the imaging sensitivity. We demonstrate efficient detection of rare, fast and

isolated cells circulating in the bloodstream with mm/s velocities.

In a second application, these QDs were also used as a sensing platform. Their fluorescence lifetime could be controllably modulated through energy transfer with proximal fluorescent dyes or quenchers. When these quenchers are conjugated to the QDs via an enzymatic substrate, the QD lifetime is shortened. Enzymatic activity cleaves the substrate, which translates into changes of the QD fluorescence lifetime. This enables near infrared, autofluorescence-free, ratiometric imaging of enzymatic activity.

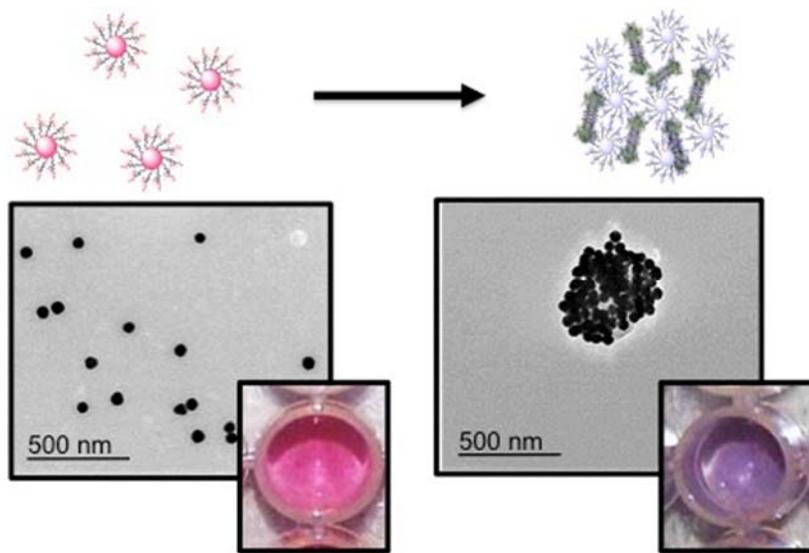
COLL 687

Glycosylated gold nanoparticle biosensors: Detection of toxins, bacteria and viruses

Sarah-Jane Richards¹, *s-j.richards@warwick.ac.uk*, **Matthew I. Gibson**^{1,2}. (1) *Department of Chemistry, University of Warwick, Coventry, United Kingdom* (2) *Warwick Medical School, University of Warwick, Coventry, United Kingdom*

The development of new analytical tools to probe pathogenic infection processes and as point-of care diagnostics is crucial to combat the spread of infectious diseases or to detect biological warfare agents. There is a growing need for biosensors that are fast, label-free, sensitive and inexpensive. Protein-carbohydrate interactions are essential for many biological processes and dictate a range of signaling and recognition processes in biological systems, including cell–cell communication, fertilization and innate immunity. However, toxins, bacteria and viruses also exploit these interactions to gain entry into our cells.

Glycosylated gold nanoparticles that change color due to lectin-mediated aggregation may find wide applicability as biosensors of bacteria, toxins and viruses. Here we present the use of precision polymer-coated gold nanoparticles to negotiate the delicate balance between saline stability and the speed of the colorimetric readout. These simple, monosaccharide conjugated gold nanoparticles are powerful tools for probing protein-carbohydrate interactions. Using a multiplexed assay and linear discriminant analysis, differentiation between lectins and toxins such as ricin or the cholera toxin, bacterial phenotypes and viruses is demonstrated. We have shown that the color change in response to the correct glycan-lectin pairing can be determined not only spectrophotometrically but by using the simple combination of a mobile phone camera and image analysis freeware, providing an ultra-low cost route to biosensors.



Colorimetric detection of toxins, bacteria and viruses using glycosylated gold nanoparticles

COLL 688

Gold nanoparticle radiosensitization of synchronized cell populations

Benjamin P. Coughlin, benjamin.coughlin@tufts.edu, Paul T. Lawrence, E Charles H. Sykes, Charles Mace. Tufts University, Medford, Massachusetts, United States

The radiosensitization of mammalian cells by gold nanoparticles (Au NPs) is a well-established phenomenon in radiation biology. One proposed mechanism by which Au NPs enhance radiation damage is through regulation of the cell cycle, particularly by arresting cells in the radiation sensitive G₂/M phase. While sporadic examples of this phenomenon exist in the literature, a systematic study of the relationship between cell cycle and radiosensitization has not been previously shown. Here, we evaluate the radiosensitization properties of polyethylene glycol (PEG)-coated Au NPs (5 nm core diameter) in H3G HeLa cells that have been synchronized at different stages of the cell cycle by a thymidine double block. Using a combination of DNA content and mitotic index measurements, we unambiguously identify time points where >70% of cells are in G₁, S, and G₂/M phases of the cell cycle, respectively. We use flow cytometry and ICP-AES to quantify the uptake of PEGylated Au NPs as a function of cell cycle phase, which, to our knowledge, is the first such measurement for this important class of nanomaterial. Using clonogenic survival assays, we evaluate the differential sensitivity enhancement ratios (SERs) for populations synchronized in G₁, S, and G₂/M. Because many chemotherapeutic drugs act by cell cycle arrest, these results may have bearing on the successful pairing of chemotherapy, radiation therapy, and Au NP administration in cancer treatment.

COLL 689

Engineered nanozymes to catalyze site-specific bioorthogonal reactions for imaging and therapeutic applications

Riddha Das¹, *das.riddha@gmail.com*, **Akash Gupta**², **Gulen Y. Tonga**⁵, **Ryan F. Landis**³, **Tsukasa Mizuhara**⁴, **Vincent M. Rotello**⁶. (1) UMass Amherst, Amherst, Massachusetts, United States (4) Kyoto University, Kyoto-shi, Japan (5) Harvard University, Boston, Massachusetts, United States (6) Univ of Massachusetts, Amherst, Massachusetts, United States

Bioorthogonal transformation of prodrugs and profluorophores using transition metal catalysts (TMC) offers a promising strategy for imaging and therapeutic applications. However, maintaining activity and controlling the localization of TMCs make their use in biomedical applications challenging. Here we report the engineering of nanoparticles of gold nanoparticles (AuNPs) with encapsulated TMCs (nanozymes) to provide specific intra- and extracellular localization. We used membrane-penetrating cationic nanoparticles for catalysis inside and 'stealth' zwitterionic particles to limit catalysis to outside of mammalian cells. Specific localization of nanozyme activity was demonstrated through profluorophore activation. Therapeutic efficacy was demonstrated through intra- and extracellular activation of a prodrug. The ability to control nanozyme localization was further shown by targeting biofilms in a complex bio-system using a co-culture model. We designed pH-switchable nanozymes that effectively localize in the acidic microenvironment of biofilms. These nanozymes generate imaging agents through bioorthogonal activation of profluorophores inside biofilms demonstrating potential for early detection of biofilm-associated infections. Taken together, these studies demonstrate a new level of spatial control for TMC-mediated bioorthogonal catalysis for diagnostic and therapeutic purposes.

COLL 690

Electric field sensitive upconverting nanoparticles: Toward background free *in vivo* action potential imaging

Randy Mehlenbacher¹, *r.mehlenbacher@gmail.com*, **Christopher Siefe**³, **Alice Lay**², **Jennifer A. Dionne**¹. (1) Materials Science and Engineering, Stanford University, Stanford, California, United States (2) Stanford University, Palo Alto, California, United States (3) Materials Science & Engineering, Stanford University, Stanford, California, United States

Recording brain activity from the individual neuron scale to neural networks is required for fully understanding the pathology of neurological diseases and developing new treatments. Optical techniques show much promise for imaging over these length scales; however, current methods generally require genetic encoding, rely on fluorophores that blink and bleach over time, or render the brains fixed or dead. Here, we report a new platform using upconverting nanoparticles coupled to voltage sensitive

dyes to overcome limitations of current technologies. Upconverting nanoparticles use long lived f-f transitions in lanthanide ions to absorb near infrared (NIR) light and emit visible light. Owing to their passive ceramic host lattice, upconverting nanoparticles typically do not respond to external fields. To confer electric field sensitivity, we have adopted a novel core-shell structure and we couple the nanoparticles to voltage sensitive dyes. The nanoparticle core is ~5 nm NaYbF₄ to maximize NIR photon absorption. The optically excited Yb³⁺ transfers energy to emitters (e.g. Er³⁺) doped in the shell. These emitters are optically coupled to the voltage sensitive dye DI-2-ANEPEQ on the nanoparticle surface. By concentrating the emitters in the shell, they are closer to the surface dyes, increasing FRET between lanthanide and dye and thereby enhancing the voltage sensitivity. We vary the shell dimensions from 0.5 to 2 and doping concentrations from 1 to 20% to maximize brightness and voltage sensitivity, while maintaining the total system size <13 nm. In the presence of an electric field, the electronic states of the dye shift and its emission intensity decreases. This shift in the electronic states changes the coupling between the upconverters and the dye leading to spectral and intensity changes in the upconverter emission when an electric field is applied. We have measured a decrease in the upconversion intensity of ~7% under an electric field of ~125 kV/cm, comparable to the ~1-10% emission intensity change isolated dye molecules undergo in electric fields. Moreover, we measure a spectro-ratiometric change (the ratio between the green and red emission in Er³⁺) in emission of ~9% in a 125 kV/cm electric field, highlighting the sensitivity of these nanoparticles as electric field sensors for in vivo electric fields. Finally, we highlight enhancements to biostability and targeting of our nanoparticles via surface-functionalization with polymer.

COLL 691

Gold nanoparticle-polyplex electroporation in the enhancement of nucleic acid delivery

*Shuyan Huang, Xuan Liu, **Shengnian Wang**, swang@latech.edu. Chemical Engineering, Louisiana Tech University, Ruston, Louisiana, United States*

Nonviral nanoparticle vectors cannot yet become competitive over natural virus-based counterparts in many therapy strategies, which ties with their poor nanoparticle quality, slow and ineffective endocytosis-mediated cellular uptake, and undesired cytotoxicity. This may fall in the tolerance for general gene delivery applications, but definitely undesired in vaccine or reprogramming type of applications as high, quick transfection and high cell viability is essential to their success. We develop new AuNP-Polyplex Electroporation based new delivery route, in which (1) monodispersed gold nanoparticles (AuNPs) are used to provide controlled assembly domain and environment with precise management on molecule interactions to obtain homogeneous polyplex in size, structure, and component quantity; (2) AuNPs also help fix free and dissociated cationic polymer to reduce their cytotoxicity and enhance electroporation based delivery route; (3) electroporation is adopted to bypass the slow and inefficient endocytosis process and to promote direct cytosolic delivery and quick nuclear entry. In

this hybrid approach, AuNPs of various sizes are first coated with polyethylenimine (PEI), which are further conjugated with DNA plasmids or siRNA molecules to form AuNPs-polyplex. The hybrid nanoparticles are then mixed with cells for electroporation treatment. The delivery efficiency is evaluated with K562 cells, showing 1.5~2 folds improvement on the transfection efficiency and no significant increase of toxicity when compared to free plasmid delivery by electroporation alone. To help reveal the assembly and release dynamics, dissipative particle dynamics (DPD) simulation and coarse-grained models are coupled to reveal the encapsulation and release details of siRNA in different polymers/AuNPs systems. The computational results are further compared to the experimental observations. With wise control strategy on the assembly quality, we anticipate such combination of physical and chemical delivery concept may stimulate further exploration in the delivery of various therapeutic materials for both in vitro and in vivo applications in vaccine or reprogramming type of applications.

COLL 692

High content analysis (HCA) of nanoparticle uptake by mammalian cells and their effects on motility, proliferation and viability

Alessia Pallaoro^{1,2}, apallaoro@chem.ucsb.edu, Wieslawa H. Dragowska², Byron D. Gates³, Donald T. Yapp^{2,4}. (1) Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada (2) Experimental Therapeutics, BC Cancer Research Centre, Vancouver, British Columbia, Canada (3) Dept of Chemistry, Simon Fraser Univ, Burnaby, British Columbia, Canada (4) Faculty of Pharmaceutical Sciences, University of British Columbia, Vancouver, British Columbia, Canada

The fate of nanoparticles (NPs) in cells and tissues, and the pathways they interact with are important factors that can indicate their potential for success as a nanotherapeutic. Standard *in vitro* cytotoxicity assays often do not predict *in vivo* therapeutic performance, because such assays capture only an average, singular aspect of the cells within the complex biological environment of culture. In contrast, high content analysis (HCA) collects and analyzes multi-parameter data from single cells in a population. The data reflect the biological status of the cells and permits sub-populations to be delineated. HCA, therefore allows to draw a more comprehensive and nuanced picture of the cell population under investigation. HCA is the “gold standard” in drug discovery for high throughput screening of drug candidates, and has been shown to accurately predict *in vivo* acute toxicities. Likewise, using HCA techniques to evaluate NPs *in vitro* may also better predict the *in vivo* efficacy and toxicity of NP therapeutics. NP uptake efficiency and toxic effects are known to depend on their charge, surface chemistry, and chemical composition. Here, we use HCA to characterize the uptake of gold nanoparticles (AuNP) presenting different surface chemistries (carrying receptor-targeting peptides vs untargeted) and evaluate their effect on cell motility, viability, and proliferation rate under short-term and long-term exposure. Through HCA we unravel some of the mechanistic aspects that govern the interaction of nanomaterials with cancer cells, by tracking fluorescently tagged NPs added to cells in culture in a 96 well plate format. Cells were stained with up to four dyes (e.g., a nuclear stain, for live and

dead cells, and a fourth dye for a parameter of interest), and imaged live. Images were subsequently analyzed to extract parameters of interest, such as the number of cells, number of NP per cell, percent dead cells, nuclear area, and intensity. The quantitative data were then evaluated in their entirety to correlate them to the biology of interest.

COLL 693

UV-visible spectroscopy-based quantification of biomolecules bound to nanoparticles

Brandi L. Baldock¹, baldockb@merrimack.edu, Jim E. Hutchison². (1) Chemistry & Biochemistry, Merrimack College, North Andover, Massachusetts, United States (2) University of Oregon, Eugene, Oregon, United States

Nanoparticles are of great interest as potential diagnostic, therapeutics, biosensing and drug delivery agents, yet many questions remain regarding their interactions with biological systems. Biomolecules such as DNA sequences and proteins that are bound to the surface of a nanoparticle determine its cellular uptake and reactivity. To tailor the properties of nanoparticles for specific applications, quantitative information regarding their interactions with biomolecules is required. Conventional methods used to determine the number of biomolecules bound to nanoparticles required that they be fluorophore labeled, which can affect their surface coverage and reactivity.

In this presentation, a rapid and convenient UV-visible based method that can be used to determine the number of DNA strands attached to nanoparticles of different core diameters will be described. When this method is used in tandem with a fluorescence dye assay, it is possible to determine the ratio of two unlabeled sequences of different lengths bound to the nanoparticles. The use of this method to determine the number of proteins bound to nanoparticles will also be discussed.

COLL 694

Understanding the interfacial events of stimuli responsive nanomaterials for the treatment of bacterial infection

Damayanti Bagchi, damayanti.bagchi@gmail.com, Samir Pal. SNBNCBS, Kolkata, India

Appropriate localization and the structure-functional integrity of a drug in a nanoscopic delivery agent essentially dictate the efficacy of the vehicle and the medicinal activity of the drug. In the case of a phototherapeutic drug, its photoinduced dynamics becomes an added parameter. The interaction at the nano-bio interface plays the vital role for the enhanced efficiency. Here, we have first explored the photoinduced dynamical events of a model phototherapeutic drug psoralen (PSO) in a potential delivery vehicle called ethosome. Moreover, NIR light activated nanohybrid comprising a nanoparticle conjugated with drug is evaluated for light mediated antimicrobial therapy. The

interfacial charge transfer properties are evaluated in details using various spectroscopic tools. Finally, the efficacies of these colloidal nanosystems have been investigated for potential antimicrobial and anti-biofilm activity.

COLL 695

Biodegradable nanocomposite antimicrobials for the eradication of multidrug-resistant bacterial biofilms without accumulated resistance

Cheng Hsuan Li¹, chenghsuanli@umass.edu, Ryan Landis¹, Akash Gupta¹, Yi-Wei Lee¹, Jessa M. Makabenta¹, Mahdieh Yazdani¹, Nipaporn Ngernyuang², Ismail Altinbasak³, Sanaa Mansoor³, Muhammadaha Areeb Shaukat Khichi³, Amitav Sanyal³, Vincent M. Rotello¹. (1) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Chulabhorn International College of Medicine, Thammasat University, Pathum Thani, Thailand (3) Chemistry, Bogazici University, Istanbul, Turkey

Multi-drug resistant bacteria infect more than 2 million people each year in the United States. These infections can often result into a chronic diseased state due to the formation of biofilms. Phytochemicals exhibit broad-spectrum activity against drug-resistant bacteria, however poor solubility of these phytochemicals in aqueous solution limits their therapeutic application. Here, we present polymer-stabilized phytochemical nanocomposites that exhibit broad-spectrum activity against multi-drug resistant bacteria and bacterial biofilms. These nanocomposites were stable in physiological condition and can be degraded in the presence of glutathione/esterase to prevent the vehicle accumulation. Furthermore, they show minimal toxicity towards mammalian cells and cannot trigger the development of drug resistance from bacteria in a serial passaging study, making these nanocomposites a promising solution to the biofilm infections and multi-drug resistant bacteria.

COLL 696

Development of targeted nanomedicines via machine learning processes

Daniel A. Heller^{1,2}, hellodan1@gmail.com, Yosi Shamay¹, Janki Shah¹, Mehtap Isik¹, Januka Budhathoki-Uprety³, Daniel Roxbury⁴, Ramya Sridharan^{1,2}, John D. Chodera⁵, Scott W. Lowe^{1,2}. (1) Memorial Sloan Kettering Cancer Center, New York, New York, United States (2) Weill Cornell Medical College, New York, New York, United States (3) Molecular Pharmacology, Memorial Sloan Kettering Cancer Center, New York, New York, United States (4) Chemical Engineering, University of Rhode Island, Kingston, Rhode Island, United States (5) Computational Biology, Memorial Sloan Kettering Cancer Center, Berkeley, California, United States

Development of targeted nanoparticle drug carriers often requires complex synthetic schemes involving both supramolecular self-assembly and chemical modification. These processes are generally difficult to predict, execute, and control. We describe

herein a targeted drug delivery system that is accurately and quantitatively predicted to self-assemble into nanoparticles based on the molecular structures of precursor molecules, which are the drugs themselves. The drugs assemble with the aid of sulfated indocyanines into particles with ultrahigh drug loadings of up to 90%. We devised quantitative structure-nanoparticle assembly prediction (QSNAP) models to identify and validate electrotopological molecular descriptors as highly predictive indicators of nano-assembly and nanoparticle size. The resulting nanoparticles selectively targeted kinase inhibitors to caveolin-1-expressing human colon cancer and autochthonous liver cancer models to yield striking therapeutic effects while avoiding dose-limiting toxicities. This finding enables the computational design of nanomedicines based on quantitative models for drug payload selection.

COLL 697

Genetically encoded acousto-magnetic protein nanostructures for non-invasive imaging of cellular functions

George J. Lu¹, *george.jiaozhi.lu@gmail.com*, *Arash Farhadi¹*, *Jerzy O. Szablowski¹*, *Audrey Lee-Gosselin¹*, *Samuel R. Barnes²*, *Anupama Lakshmanan¹*, *Raymond W. Bourdeau¹*, *Mikhail G. Shapiro¹*. (1) *California Institute of Technology, Pasadena, California, United States* (2) *Loma Linda University, Loma Linda, California, United States*

Genetically encoded optical reporters such as green fluorescent protein (GFP) have revolutionized biomedical research by enabling observations of specific biological processes in engineered cells and transgenic animals. However, such optical agents are fundamentally limited by the ~ 1 mm penetration depth of light in opaque tissues. As cellular therapies advance towards rodent models and ultimately humans, this limitation becomes increasingly severe. Therefore, we aim to develop new classes of reporter genes for non-invasive imaging modalities that utilize deeply penetrant forms of energy, such as magnetic fields and sound waves. Here, we describe the first reporter genes for acoustically modulated magnetic resonance imaging (AM-MRI), a modality that combines MRI and ultrasound. These agents are based on gas vesicles (GVs), a class of gas-filled protein nanostructures evolved in photosynthetic microbes as a means to regulate their buoyancy. GV s are hundreds of nanometers in size, and transferring the gene cluster into *E. coli* enables their formation inside these bacteria. The air inside GV s allows them to be detected at nanomolar concentrations by susceptibility-based MRI. Uniquely, such contrast is “erasable” by ultrasound pulses at specific pressures, which permits selective imaging of these agents without background tissue contrast that has plagued the use of existing MRI contrast agents. Furthermore, gene orthologs encode GV s of different size, shape and ultrasound-responsive pressure, which in turn give rise to differential MRI contrast and “erasable” pressure thresholds. Thus, multiplexed imaging can be achieved by genetically encoding several types of GV s. Finally, the clustering of GV s induces a 10-fold enhancement of T2* contrast, which enables the potential design of sensors to dynamically report biological signals. The ability of GV s to be genetically encoded and engineered opens the possibility of using

this new form of imaging contrast in a wide range of applications, especially in diagnosis and cellular therapeutics.

COLL 698

Photothermal intracellular delivery using large-area Au nanodisk arrays fabricated by chemical lift-off lithography

Chuanzhen Zhao¹, chuanzhenzhao@gmail.com, Tianxing Man², Xiaobin Xu^{1,3}, Qing Yang¹, Wenfei Liu¹, Steven J. Jonas⁴, Michael A. Teitell⁵, Anne M. Andrews^{1,6}, Pei-Yu Chiou^{2,7}, Paul S. Weiss^{1,8}. (1) California NanoSystems Institute, Department of Chemistry & Biochemistry, UCLA, Los Angeles, California, United States (2) Department of Mechanical and Aerospace Engineering, UCLA, Los Angeles, California, United States (3) School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore (4) California NanoSystems Institute, Department of Pediatrics, David Geffen School of Medicine, Eli & Edythe Broad Center of Regenerative Medicine and Stem Cell Research, Children's Discovery and Innovation Institute, UCLA, Los Angeles, California, United States (5) California NanoSystems Institute, Department of Bioengineering, Department of Pathology and Laboratory Medicine, Division of Dermatology, Department of Medicine, Department of Molecular and Medical Pharmacology, Jonsson Comprehensive Cancer Center, and Broad Stem Cell Research Center, UCLA, Los Angeles, California, United States (6) Department of Psychiatry and Biobehavioral Health, Semel Institute for Neuroscience and Human Behavior, and Hatos Center for Neuropharmacology, UCLA, Los Angeles, California, United States (7) Department of Bioengineering, UCLA, Los Angeles, California, United States (8) Department of Materials Science and Engineering, UCLA, Los Angeles, California, United States

High-efficiency intracellular delivery is at the heart of the future personalized medicine, with promising applications that include gene editing and modification, intracellular imaging, and drug delivery. Non-viral intracellular strategies have garnered significant attention to achieve high delivery efficiencies and increase cell viabilities, as well as to lower the costs compared with viral-based methods. Photothermal strategies, which use metal plasmonic structures and cavitation bubbles induced by nanosecond laser pulses, have made great strides towards achieving these goals. However, the fabrication process is complicated and hampered by low throughput. Here, we demonstrate the use of large-area arrays of plasmonic gold nanodisks for photothermal intracellular delivery. The Au nanostructures were fabricated using chemical lift-off lithography, which is a large-area, high-throughput, and low-cost patterning strategy developed recently in our group. In this way, nanostructures have been fabricated on a variety of substrates (e.g., petri dishes) that facilitate *in situ* intracellular delivery in laboratory cell culture environments, demonstrating the ability to integrate this technique with existing medical devices. Nanosecond laser pulses were used to excite the plasmonic nanostructures and locally heat their surroundings, thereby creating transient pores in cell membranes that enable the delivery of biomolecular payloads. Devices were optimized by varying the size and spacing of the Au nanodisks as well as the incident pulse intensity. In doing

so, we achieved delivery of 0.6 kDa Calcein into cells with efficiencies of up to 95% and cell viabilities up to 98%.

COLL 699

Rapid sequential *in situ* multiplexing with DNA exchange imaging

Peng L. Yin, *peng_yin@hms.harvard.edu*. Wyss Institute, Boston, Massachusetts, United States

To decipher the molecular mechanisms of biological function, it is critical to map the molecular composition of individual cells or even more importantly tissue samples in the context of their biological environment *in situ*. Immunofluorescence (IF) provides specific labeling for molecular profiling. However, conventional IF methods have finite multiplexing capabilities due to spectral overlap of the fluorophores. Various sequential imaging methods have been developed to circumvent this spectral limit but are not widely adopted due to the common limitation of requiring multirounds of slow immunostaining. We present here a practical and robust method, which we call DNA Exchange Imaging (DEI), for rapid *in situ* spectrally unlimited multiplexing. This technique overcomes speed restrictions by allowing for single-round immunostaining with DNA-barcoded antibodies, followed by rapid (less than 10 min) buffer exchange of fluorophore-bearing DNA imager strands. The programmability of DEI allows us to apply it to diverse microscopy platforms (with Exchange Confocal, Exchange-SIM, Exchange-STED, and Exchange-PAINT demonstrated here) at multiple desired resolution scales (from ~300 nm down to sub-20 nm). We optimized and validated the use of DEI in complex biological samples, including primary neuron cultures and tissue sections. These results collectively suggest DNA exchange as a versatile, practical platform for rapid, highly multiplexed *in situ* imaging, potentially enabling new applications ranging from basic science, to drug discovery, and to clinical pathology.

COLL 700

Small platform enables big change – Nanotech-assisted discovery of novel biomarkers for disease diagnosis

Tony Hu, *tyhu@asu.edu*. Biodesign Institute, Arizona State University, Tempe, Arizona, United States

Most TB cases are diagnosed by slow and non-specific microbiological methods. PCR-based GeneXpert MTB/RIF, introduced to improve speed and specificity, has poor sensitivity at low bacterial loads, cannot distinguish live and nonviable bacilli, and has reduced performance in HIV/TB co-infected patients. Serum-based detection of *Mtb* virulence factors offers direct evidence of TB, but current methods lack adequate sensitivity and specificity. We have developed a blood-based assay for rapid, specific, and high-sensitivity TB diagnosis, which uses nanodisks to enrich *Mtb*-selective peptides from serum samples. Our approach incorporates several technical advances,

including identification of strongly *Mtb*-selective antigen peptides, and development of antibody-conjugated nanodisks that markedly increase target peptide enrichment and laser desorption/ionization of nanodisk-bound peptides to enhance their detection. This approach disrupts protein complexes, releasing *Mtb* antigen likely missed by conventional immunoassays targeting intact *Mtb* proteins. In addition, the assay addresses sensitivity and speed shortcomings associated with active TB diagnosis, and meets several criteria for a WHO-mandated noninvasive TB assay. Specifically, it (i) uses a small, noninvasive specimen; (ii) does not require bacterial isolation; (iii) has high sensitivity and specificity for active TB cases in extrapulmonary, culture-negative, and HIV-infected TB patients, where diagnosis often requires multiple tests, including invasive procedures. It also (iv) directly quantifies *Mtb* antigens for rapid monitoring of anti-TB therapy effects; (v) uses a streamlined process amenable to high-throughput operation in clinical and research settings; and (vi) can be performed using equipment already approved by the Food and Drug Administration for other diagnostic assays. To further expand the capability of the assay in serving the patients in resource-limited area, we have also developed the solid-state nanopore technology, which can recognize single detection events to quantify two *Mtb*-specific peptide biomarkers derived from blood samples, to develop a point-of-care diagnostic system. Based on our preliminary studies, we are confident that this diagnostic system will benefit the global tuberculosis control effort by improving the personalized management of TB.

COLL 701

Cartilage penetrating nanocarriers enhance drug delivery and efficacy in osteoarthritis

Brett Geiger¹, bgeiger@mit.edu, Sheryl Wang¹, Robert F. Padera², Alan Grodzinsky¹, Paula T. Hammond³. (1) Biological Engineering, Massachusetts Institute of Technology, Boston, Massachusetts, United States (2) Pathology, Brigham and Women's Hospital, Boston, Massachusetts, United States (3) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Osteoarthritis is a debilitating disease of the joint which manifests as a loss of articular cartilage, causing serious pain and impeding mobility. Currently, no disease modifying osteoarthritis drug (DMOAD) capable of preserving cartilage exists and the standard of care is merely palliative.

The approval of a DMOAD has been hindered by repeated clinical trial failures, due in considerable part to inadequate drug delivery to cartilage, even with local injection directly into the affected joint. Recent work has identified that cationic nanomaterials display increased binding to and penetration throughout anionic cartilage tissue via electrostatic interactions.

In this research, to develop an intra-articular drug delivery vehicle for DMOADs, we screened a small library of partially PEGylated cationic dendrimers (20-60% end group functionalization) to identify an optimally charged dendrimer with high cartilage binding

and no toxicity. The lead PEGylated dendrimer was conjugated to insulin like growth factor 1 (IGF-1) without loss in bioactivity and tested for penetration into bovine cartilage, pharmacokinetics following intra-articular injection in rats, and efficacy in a surgically induced rat osteoarthritis model.

71% of the lead dendrimer-IGF-1 conjugate incubated with bovine cartilage explants bound to the tissue within 2 days. The conjugate penetrated through the entire 1000 μm depth of the tissue, on the order of human cartilage thickness. In contrast, free IGF-1 displayed around 2% binding to the tissue and could only penetrate ~ 20 μm in 2 days.

Free IGF-1 and dendrimer-IGF-1 were injected into rat joints and monitored by *in vivo* imaging (IVIS) over 28 days. Half-lives were calculated for each based on single phase exponential decay fits of the data. Free IGF-1 had a joint half-life of 0.41 days whereas dendrimer-IGF-1 had a joint half-life of 4.21 days, 10 times that of free IGF-1.

We evaluated if dendrimer-IGF-1 could rescue cartilage in a surgically induced rat model of osteoarthritis. 48 hours after surgery, dendrimer-IGF-1, free IGF-1, or no treatment was injected. 4 weeks later, the rats were sacrificed and quantitative measurements of cartilage and bone degeneration were taken from histology and μCT images. While IGF-1 alone was ineffective, injection of the dendrimer-IGF-1 conjugate led to significantly reduced cartilage degeneration width and osteophyte (bone spur) volume at 30 days post-surgery, relative to the untreated animals.

COLL 702

Magnetothermal neuromodulation in awake, freely moving animals

*Rahul Munshi*¹, *Shahnaz Qadri*^{1,2}, *Idoia Castellanos-Rubio*^{1,3}, ***Arnd Pralle***¹, *apralle@buffalo.edu*. (1) *Physics, University at Buffalo, Buffalo, New York, United States* (2) *Mechanical Engineering, Qatar University, Doha, Doha, Qatar* (3) *Química Inorgánica, Universidad del País Vasco, Sarriena, Leioa, Spain*

Deciphering how complex neuronal circuits control behavior and emotions requires modulating the activity of specific neurons deep inside the brain of freely behaving animals with temporal and spatial precision. Ideally, one transiently perturbs the circuitry driving a particular behavior. Here, we show how magnetothermal neuronal modulation can be realized in-vitro and in-vivo. Localized heat transfer to genetically modified or wild type neurons can excite or inhibit those cells. In radiofrequency magnetic fields, superparamagnetic particles can be tailored to act as confined low dimensional heat sources for such application. Here, we inquire how the geometrical distribution of heat sources on and around the cell membrane can facilitate signal transduction and trigger behavioral changes in mice. Tagging the nanoparticles with a fluorescent dye enabled us to systematically study the temperature evolution by monitoring fluorescence intensity changes. We explore heating of nanoparticles suspended in inter cellular spaces and compare it to two dimensional sheets of membrane targeted nanoparticles. Particles, pre-arranged in sheet configuration and

confined within polymer matrices allow for area density control and prolonged retention time. We fabricated such particle embedded polymer discs and characterized them on cells.

Then with demonstrate how neurons, heat-sensitized by expressing TRPV1 are activated with magnetic field application, and how magnetothermal genetic stimulation in the motor cortex evokes ambulation, deep brain stimulation in the striatum causes rotation around the body-axis, and stimulation near the ridge between ventral and dorsal striatum causes freezing-of-gait. The duration of the behavior correlated tightly with field application. This approach provides genetically and spatially targetable, repeatable and temporarily precise activation of deep-brain circuits without the need for surgical implantation of any device.

COLL 703

Tuning the scaffolding bionanofiber's structure and surface for electrochemically sensing cancer and normal cells

Z R. Tian^{1,3}, rtian@uark.edu, Hanan Alismail^{3,2}, Yuchun Du^{2,4}, Jianhong Zhou⁴, Jacob Koster⁵, Parker Cole^{3,5}, Laura Mantooth^{1,5}. (1) Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, United States (2) Cell and Molecular Biology, University of Arkansas, Fayetteville, Arkansas, United States (3) Biomedical Engineering, University of Arkansas, Fayetteville, Arkansas, United States (4) Biological Sciences, University of Arkansas, Fayetteville, Arkansas, United States (5) Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, Arkansas, United States

Often, an electrochemical sensor may not easily differentiate the cancerous and normal cells of the same type due to a minor difference between their surfaces, while most bioscaffolds to comfort and harbor these cells are too electrically insulating to electrochemically detect the cells and/or cancer biomarkers. Here we report a new electrochemically sensory bioscaffold of biocompatible nanofibers grown on a Ti implant surface in a simple and low-cost hydrothermal nanosynthesis able to tune the nanofiber's lattice and surface using different transition metals, as proven by their XRD, SEM-EDX, and TEM data. The new sensory bioscaffold has distinguished the normal and cancerous cells and some cancer biomarkers directly, sensitively, reproducibly and in real-time. This new cancer nanotechnology is one of the long-overdue platforms potentially applicable to the quick, simple and low-cost detections of cells and biomarkers of different types, which has been seldom reported in literature to the best of our knowledge.

COLL 704

Design of quantum dot-protein bioconjugates for extracellular control of intracellular drug release

Lauren D. Field¹, lauren.field.ctr@nrl.navy.mil, Scott Walper¹, Kimihiro Susumu^{1,3}, Guillermo Lasarte-Aragones^{1,2}, Eunkeu Oh^{1,3}, Igor Medintz¹, James Delehanty¹. (1) US Naval Research Laboratory, Washington, District of Columbia, United States (2) George Mason University, Fairfax, Virginia, United States (3) Key W Corporation, Hanover, Maryland, United States

Nanoparticle mediated drug delivery (NMDD) is a rapidly developing field aimed at improving the efficacy of therapeutics that currently rely on systemic delivery, which often produces numerous secondary side effects. NMDD aims to overcome these shortfalls by potentially increasing circulation time, adding specified targeting or incorporating visualization capabilities within one particle complex. One critical area of NMDD research focuses on the release of the drug cargo from the nanoparticle (NP) through one of three general methods: 1) passive release 2) active release facilitated *via* an environmental change (pH, REDOX) or 3) active release triggered by an external source (UV, magnetism). This research focuses on designing a new method of active cargo actuation triggered *via* the extracellular addition of a secondary molecule. Our complex utilizes quantum dots (QDs) as the central NP scaffold, with maltose binding protein (MBP) appended onto the QD surface and loaded with either a drug or dye molecule conjugated to the maltose analog beta-cyclodextrin (β CD). In choosing the QD as the central scaffold, Förster resonance energy transfer (FRET) can be used to visualize cargo release, as the 520 nm QD acts as an ideal FRET donor for both the dye, TideFluor3 (TF3), and drug, doxorubicin (DOX), chosen as cargo. Actuation of the cargo from the NP is facilitated through the addition of maltose, which competitively displaces the β CD from the MBP binding pocket. As the cargo is released, the QD photoluminescent intensity changes and the associated FRET change can be quantified. Microplate analysis of these constructs showed a dynamic response to increasing concentrations of maltose that was directly monitored as a change in FRET. The efficacy of these constructs *in vitro* was determined by microinjecting them into the cytosol of COS-1 cells and monitoring their stability and maltose-associated cargo release over time using FRET-based confocal microscopy. Our results show the potential efficacy of these self-assembled QD-MBP- β CD to facilitate *intracellular* cargo actuation through the *extracellular* addition of a well-tolerated nutrient. We anticipate that this method of extracellularly triggered cargo release will be useful for future development of *in vivo* on-demand drug delivery.

COLL 705

Functionalized thin shell microcapsule for targeted delivery and release

Liyuan Zhang¹, liyuanzhang@seas.harvard.edu, Jonathan Didier¹, Hunan Wang³, David A. Weitz². (1) Mckay Lab 517, Harvard University, Cambridge, Massachusetts, United States (2) Dept of Physics Pierce Hall, Harvard Univ, Cambridge, Massachusetts, United States (3) School of Life Science and Biotechnology, Dalian University of Technology, Shenyang, Liaoning, China

A continuously growing area of controlled tunable transport and separation of biomolecules and drugs has been attracted attention to the stimuli responsive porous hydrogel thin film. These hydrogel film can swell or shrink resulting in opening or closing of the film's pore under stimuli. Such responsive film can be used in the configuration of microcapsules with adjusted thickness and well-defined pore that response to an external signal which have wild applications, such as filtration, separation and drug encapsulation & delivery. Droplet microfluidic offers unique opportunity for producing these responsive microcapsules that fill the demands. We have fabricated a thin-shell microcapsules encapsulation system by microfluidic technique. This microcapsule with ultra-thin shell that can response multiple stimuli such as temperature, ionic strength and osmotic pressure. We also explore their application in controlled delivery and target release.

COLL 706

Encapsulation, protection and programmed release of retinol from silicone particles for topical applications

Wyatt Shields^{1,2}, cshields723@gmail.com, John P. White², Erica G. Osta², Jerishma Patel², Shashank Rajkumar², Stefan Zauscher². (1) School of Engineering & Applied Sciences, Harvard University, Cambridge, Massachusetts, United States (2) Mechanical Engineering & Materials Science, Duke University, Durham, North Carolina, United States

New active pharmaceutical ingredients (APIs) are developed each year to address major challenges in skin care (e.g., for treating psoriasis, eczema and various carcinomas). However, many of these APIs fail to impact current dermatological practices due to the instability, poor solubility and/or narrow therapeutic windows of the APIs, leading to limited therapeutic benefits, or in some cases, deleterious side effects. While some have looked to microencapsulation to overcome these challenges, current technologies fail to meet all of the key demand drivers: increased stability of API, controlled release of the API, low cost, size control of the delivery platform, high payloads, regulatory compliance, and marketability. To address these needs, we have developed a highly scalable process to synthesize programmable silicone particles via sol-gel chemistry that enables direct control over the release of APIs. Our process allows us to control the size (i.e., 0.15 to 15 μm) and stiffness of the particles (600 MPa to 2.50 GPa), while maintaining a narrow size distribution (i.e., C.V. <15%), even when scaling the reaction up to gallons at a time, which is critical for manufacturing and standardization. We have shown that the particles can encapsulate retinol (a proof-of-concept molecule used in the skin care industry that is highly sensitive to breakdown from light and oxygen) with efficiencies up to 85%, that our particles can protect retinol from degradation 9x longer than unencapsulated retinol, and that our particles can slowly release retinol over several hours, thus leading to less irritation (23% less irritation on human skin compared to a predicate technology). Importantly, we will discuss how modifying the composition of the particles (i.e., crosslink density) through regulating the silane monomers used in the reaction imparts the ability to tune the

release rate of APIs over two orders of magnitude. These findings reveal that these particles can encapsulate, protect and controllably release retinol and a variety of hydrophobic APIs limited by narrow therapeutic windows. We will show that this technology can be used to encapsulate prescription drugs (i.e., ingenol mebutate, brand name Picato®, which is for treating actinic keratosis) with efficiencies up to 70%. We will also show that these particles have been used to encapsulate fluorescent dyes, antioxidants and pesticides, establishing this technology as a true platform technology.

COLL 707

Specific targeting of ovarian tumor associated macrophages by large, anionic nanoparticles

Jacob M. Berlin, jberlin@coh.org. Molecular Medicine, Beckman Research Institute at City of Hope, Duarte, California, United States

Immunotherapy is emerging as one of the most effective methods for treating many cancers. However, immunotherapy can still introduce significant off target toxicity and methods are sought to enable targeted immunotherapy at tumor sites. Here, we show that relatively large (>100 nm), anionic nanoparticles administered IP selectively accumulate in tumor associated macrophages (TAMs). In a mouse model of ovarian cancer, fluorescently labeled silica and polystyrene nanoparticles administered intraperitoneally were exclusively found in TAMs. Quantifying silica particle uptake indicated that >70% of the injected dose was in TAMs. Particles that were smaller than 100 nm or cationic or administered IV showed no TAM targeting. Moreover, this phenomenon is likely to occur in humans because when freshly excised human surgical samples were treated with the fluorescent silica nanoparticles no interaction with healthy tissue was seen but selective uptake by TAMs was seen in many different patient samples. Ovarian cancer is a deadly disease that afflicts approximately 22,000 women per year in the US and the presence of immunosuppressive TAMs at tumors is correlated with decreased survival. The ability to selective target TAMs opens the door to targeted immunotherapy for ovarian cancer.

COLL 708

Ligand design, synthesis and formulation for gold nanoparticle stabilization, targeting, drug loading and controlled release: Towards new multi-ligand targeted nanoplatforms for doxorubicin delivery

Utpal K. Mondal¹, tuf08263@temple.edu, Ahmed Shabana¹, Md R. Alam¹, Taylor Spoon¹, Codee A. Ross¹, Madesh Muniswamy², Claudiu T. Supuran³, Marc A. Ilies¹. (1) Pharmaceutical Sciences, Temple University School of Pharmacy, Philadelphia, Pennsylvania, United States (2) Biochemistry, Temple University School of Medicine, Philadelphia, Pennsylvania, United States (3) Univ Florence Lab Chim Bioorg, Sesto Fiorentino, Italy

Gold nanoparticles (Au NPs) have emerged as a robust and versatile platform technology for diagnostic and delivery purposes during recent years, due to their unique physicochemical and optical properties and excellent biocompatibility. Using ligands strategically designed against epitopes expressed on cells in pathological states, as well as various drug conjugates, Au NPs can function as targeted delivery systems in the detection and treatment of various dysfunctions and diseases, including cancer. We will present our recent results towards the design of various compatible gold nanoparticle ligands for enhanced colloidal stability, targeting, drug loading and controlled release. Special emphasis will be dedicated to formulations strategies to ensure ligand stability, high drug loading and optimum targeting and stability of the gold nanoparticles. Relevant biological data emphasizing the ability of the resulted gold nanoplatforms to function as stable and efficient delivery systems for doxorubicin will also be presented.

COLL 709

Integration of inorganic nanomaterials within biological systems using a coordinating polymer coating

*Liang Du, Wentao Wang, Zhicheng Jin, **Hedi M. Mattoussi**, mattoussi@chem.fsu.edu. Chem Biochem, Florida State University, Tallahassee, Florida, United States*

Colloidal inorganic nanocrystals, grown via solution phase reactions, have dimensions of ~1-100 nm, a size regime that is comparable to those of biomolecules. Nanocrystals made of semiconductor, metal and metal oxide cores exhibit unique photo-physical properties not shared by their bulk parent materials. These materials offer great promises for use as in vivo and in vitro platforms in biomedical applications. We have developed a new set of multifunctional, metal-coordinating polymers that are optimized for surface functionalizing a variety of inorganic nanocrystals. The ligand design exploits the effectiveness of the one-step nucleophilic addition reaction to introduce several anchoring groups, hydrophilic or hydrophobic moieties and reactive functionalities into a single polymer chain. In particular, we have shown that, in addition to luminescent quantum dots, these ligands can be applied to functionalize iron oxide nanocrystals, Au nanoparticles, Au nanorods, and Au nano-shells and Au nano-stars alike. This surface-functionalization strategy promotes steric stabilization of the nanocrystals over a wide range of conditions. It also yields compact and reactive platforms, while preventing corona formation in biological media. Characterization of the coating relied on NMR as well as other spectroscopy techniques. We have further used the resulting hydrophilic platforms to develop a range of applications, which include biosensor design and live cell imaging.

COLL 710

Self-assembled fluorinated quantum dots as a novel delivery platform for enzymes

Carolina Carrillo Carrion¹, *carolcc83@hotmail.com*, **Monica Carril**², **Wolfgang Parak**³. (1) *BioNanoTools Lab, CiQUS, University Santiago de Compostela, Santiago de Compostela, Spain* (2) *CIC biomaGUNE, San Sebastian, Spain* (3) *CHyN, Universitaet Hamburg, Hamburg, Germany*

Self-assembled nanoparticles are considered as one of the most promising nanosystems to deliver drugs and biological molecules such as enzymes for therapeutic applications. Non-covalent hydrophobic interactions play an important role in the formation of assemblies, and fluorine-fluorine interactions are particularly interesting because the unique hydrophobicity and lipophilicity of fluorine lead to stronger interactions. Herein, inspired by the role of fluorine in self-assembly and its favorable interaction with proteins, we report a novel delivery platform for enzymes based on the formation of nanoassemblies of fluorinated quantum dots. The obtained nanoassemblies with a size of around 50 nm presented very good colloidal stability in the presence of diverse ions up to 500 μ M, in a wide range of pH (from 5 to 9) and over the time. These nanoassemblies were able to encapsulate different enzymes (laccase and α -galactosidase) obtaining high loading efficiencies. Importantly, the encapsulated enzymes maintained their catalytic activity following a Michaelis-Menten kinetic. Under acidic environment (as in endosomes/lysosomes), they were slowly disassembled allowing the release of enzymes. 50% of encapsulated enzyme was released within 24 h, and importantly the enzymes retained their activity after release. The main achievements of this work are: (i) Proof of the potential of non-covalent fluorine-fluorine interactions as driving force for the self-assembly of NPs, and (ii) Demonstration of the ability of this system to carry and deliver enzymes in a controlled fashion.

COLL 711

Preparation and quantification of various degrees of hydrophobic glass surfaces

Sushobhan Pradhan, *pradhan.sushobhan27@gmail.com*, **Prem K. Bikkina**. *School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, United States*

The wetting nature of solid surfaces has numerous industrial applications ranging from enhanced oil (petroleum) recovery to microelectronics manufacturing. Wettability of an inert solid surface is its relative affinity towards a fluid in the presence of another immiscible or sparingly soluble fluid. Contact angle measurement is a widely used and accepted method for quantifying wettability of a surface. Alteration of inherently hydrophilic glass/quartz surface towards hydrophobic nature has many applications especially in microfluidics. The current study presents experimental procedures to obtain various degrees of controlled hydrophobicities on glass surfaces, corresponding air-water contact angle and surface roughness measurements using goniometer and atomic force microscopy, respectively. Chlorinated Polydimethylsiloxane (CM), Chlorinated Fluoroalkylmethylsiloxane (CF) and Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)Triethoxysilane (HT) with the respective experimental protocols were used to prepare the hydrophobic surfaces. First, all the glass substrates were rinsed in

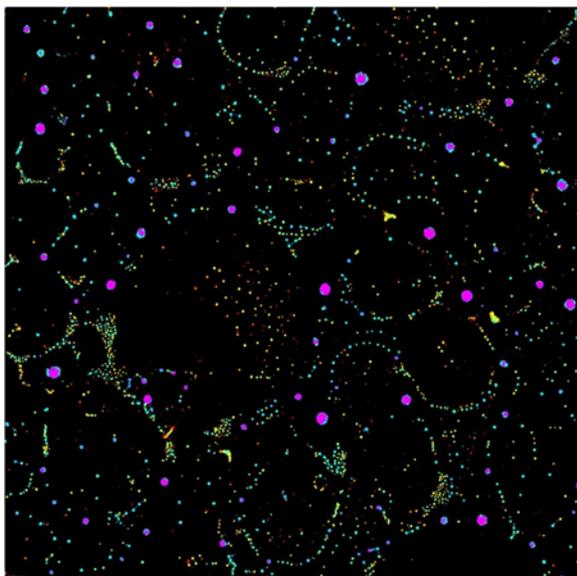
toluene. Then the silane (HT) was dissolved in 95:5 volume percent ethanol:water mixture and a 0.02% by volume glacial acetic acid and the siloxanes (CM and CF) were dissolved in toluene. Subsequently, the substrates were added to the respective solutions and left in the solutions for an hour for the surface chemical reactions to occur. To remove unreacted silane and siloxanes, the substrates were rinsed in ethanol, and n-hexane and ethanol, respectively. The untreated substrates were rinsed using n-hexane and ethanol. The treated and untreated substrates were dried in an oven at 105 °C. The average air-water contact angles measured on CM, CF, and HT hydrophobic surfaces were $90.8 \pm 0.8^\circ$, $97.8 \pm 0.4^\circ$, and $114.6 \pm 0.75^\circ$, respectively, whereas on the untreated hydrophilic glass surface the contact angle was $33.91 \pm 0.4^\circ$. The surface roughness data on the treated and untreated surfaces were found to be in the range of 1-5 nm. It is a known fact that on smooth surfaces such as used in this study, the maximum attainable air-water contact angle is 120° . So, the HT treated glass surface wettability alteration is close to the maximum possible hydrophobicity. From the above measurements, it can be observed that the contact angle values on treated glass surfaces are increased by 57° to 82° compared to the untreated surface depending on the coating material.

COLL 712

Optical characterization of surface adlayers and their compositional demixing at the nanoscale

Limin Xiang¹, lxiang2@berkeley.edu, Michal Wojcik¹, Samuel Kenny¹, Rui Yan¹, Seonah Moon¹, Wan Li¹, Ke Xu^{1,2}. (1) Department of Chemistry, University of California, Berkeley, Berkeley, California, United States (2) Chan Zuckerberg Biohub, San Francisco, California, United States

Under ambient conditions, the behavior of a solid surface is often dominated by a molecularly thin adsorbed layer (adlayer) of small molecules. Here we develop an optical approach to unveil the nanoscale structure and composition of small-molecule adlayers on glass surfaces through spectrally resolved super-resolution microscopy. By recording the images and emission spectra of $\sim 10^6$ individual solvatochromic molecules that turn fluorescent in the adlayer phase, we obtain ~ 30 nm spatial resolution and achieve concurrent measurement of local polarity. This allows us to establish that the adlayer dimensionality gradually increases through a sequence of 0D (nanodroplets), 1D (nano-lines), and 2D (films) for liquids of increasing polarity. Moreover, we find that in adlayers, a solution of two miscible liquids spontaneously demixes into nanodroplets of different compositions that correlate strongly with droplet size and location. We thus reveal unexpectedly rich structural and compositional behaviors of surface adlayers at the nanoscale.



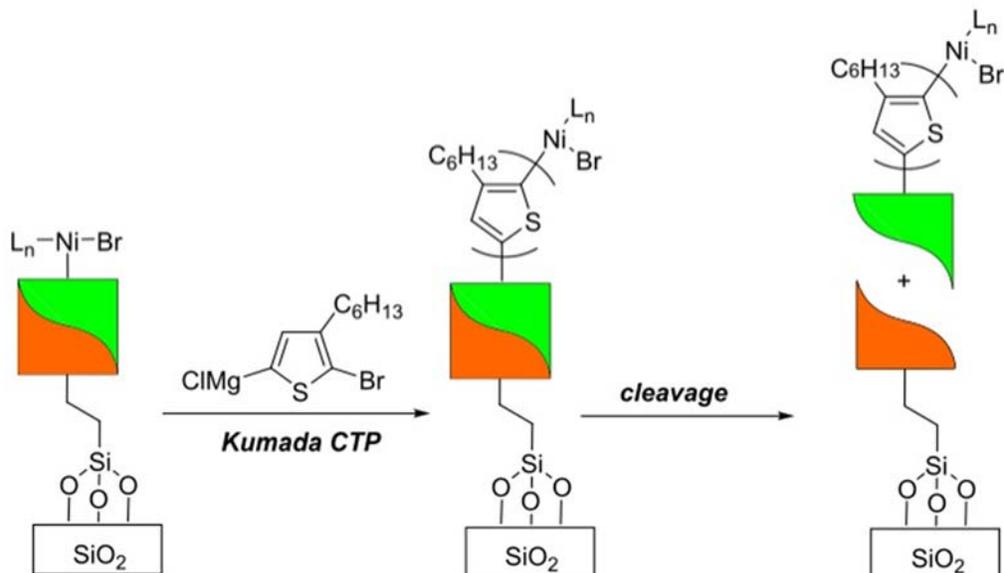
Nanoscale decomposition of a two-component mixture (trichloroethylene and chloroform) on the surface. Color indicates the percentage of chloroform.

COLL 713

Development of a self-assembled monolayer that is cleavable under mild conditions for surface-grafted conjugated polymers

Pamela M. Lundin, *pamelajournals1@gmail.com*. Department of Chemistry, High Point University, High Point, North Carolina, United States

The development of catalyst-transfer polycondensation (CTP) has enabled the synthesis of sophisticated conjugated polymers (CP) architectures, such as surface-grafted CPs. To do this, the surface is modified with a self-assembled monolayer (SAM) that is then functionalized with a metal(II) complex, which serves as the catalytic initiator for growth of the polymer. One common surface that has been used for these surface-grafted CPs is silica. However, after polymerization, de-grafting from the silica surface requires the use of the toxic strong acid HF. We have designed an alternative silane structure for creating a SAM capable of surface-initiated CTP, but which can be easily cleaved in its middle using mild reagents rather than at the siloxy-functionalized surface using HF. We present our preparation of the SAM functionalized with a Ni(II) complex through oxidative insertion of Ni(dppp)₂ into the terminal aryl halide functionality. This Ni-functionalized SAM initiates a Kumada CTP of (5-bromo-4-hexylthiophen-2-yl)magnesium chloride to prepare surface-grafted poly(3-hexylthiophene). The SAM grafting the polymer to the surface is then cleaved under mild conditions. Atomic force microscopy, scanning electron microscopy/energy-dispersive X-ray spectroscopy, and contact angle measurements are used to characterize the surface before and after cleavage. The liberated polymer is examined by NMR spectroscopy and molecular weight determination.



COLL 714

Chain-length dependent reactivity of thiolate self-assembled monolayers with atomic gas species

Sarah Brown, sbrown15@uchicago.edu, Jeffrey Saylor, Steven J. Sibener. Chemistry, The University of Chicago, Chicago, Illinois, United States

Thiolate self-assembled monolayers (SAMs) provide platforms for easily customisable organic interfaces, making them an excellent model system for studying the chemical properties of organic thin films. In particular, their reactions with atomic gas species such as hydrogen and oxygen yield important information about gas-surface interactions in organic films, how static and dynamic disorder influence passivation, as well as various hydrogenation and oxidation reactions. We are currently investigating the reactions of these SAMs with atomic hydrogen (H), using an angle-directed atomic gas source and *in situ* ultra-high vacuum scanning tunnelling microscopy (UHV-STM). First, a series of alkanethiolate samples of varying chain length (6 to 11 carbon atoms long) were reacted with H, resulting in the monolayers' conversion from close-packed standing-up phase to lower density lying-down phase. Regardless of chain length or even-/oddness, which were expected to impact the effectiveness of H penetration into the monolayer due to differences in the chains' lateral mobility and terminal structure, all samples exhibited common kinetic mechanistic details. The relative reaction rates of different chain lengths were obtained using simultaneous dosing of multiple samples. Second, a close-packed 1H,1H,2H,2H-perfluorodecanethiol SAM (a fluorinated analog of the 1-decanethiol SAM) was reacted with H. Dosing this sample under the same conditions as the 1-decanethiol sample revealed little to no reactivity. Ongoing studies continue to explore the reactivity of this family of saturated SAM systems including investigation of the kinetics and mechanism of the lying-down phase's reactivity with H.

Further investigations involving atomic oxygen and different SAM chemical compositions and structures will follow.

COLL 715

Probing curvature effects of surfactant adsorbing onto liquid/vapor interfaces of water using Monte Carlo simulations

Mona S. Minkara¹, *mona.minkara@gmail.com*, **Connor L. Venteicher**¹, **Jingyi L. Chen**¹, **Bai Xue**¹, **J I. Siepmann**^{1,2}. (1) *Chemistry and Chemical Theory Center, University of Minnesota, Minneapolis, Minnesota, United States* (2) *Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States*

Cavitation formation around and on propellers of submarines affects propulsive efficiency, can cause blade damage, and influences the wake signature. Therefore, understanding the effect surfactants have on the structure of water bubbles and how the surfactant enrichment changes with varying interfaces is important for naval research. Here, we propose the study of surfactants adsorbing onto different liquid/vapor interfaces of water; we aim to observe how the concentration of surfactant adsorbed at different interfaces of water varies. We leverage Monte Carlo simulations in the NpT osmotic Gibbs ensemble. In our method, we setup four thermodynamically connected simulation boxes; one contains a bubble of water, one contains a film of water, one contains a bulk water phase, and the last contains a vapor reservoir of the surfactant of interest, ethanol. We only allow the ethanol molecules to swap between the four boxes. The water and ethanol molecules are modeled with the TIP4P/2005 and TraPPE-UA force fields, respectively, for computational accuracy.

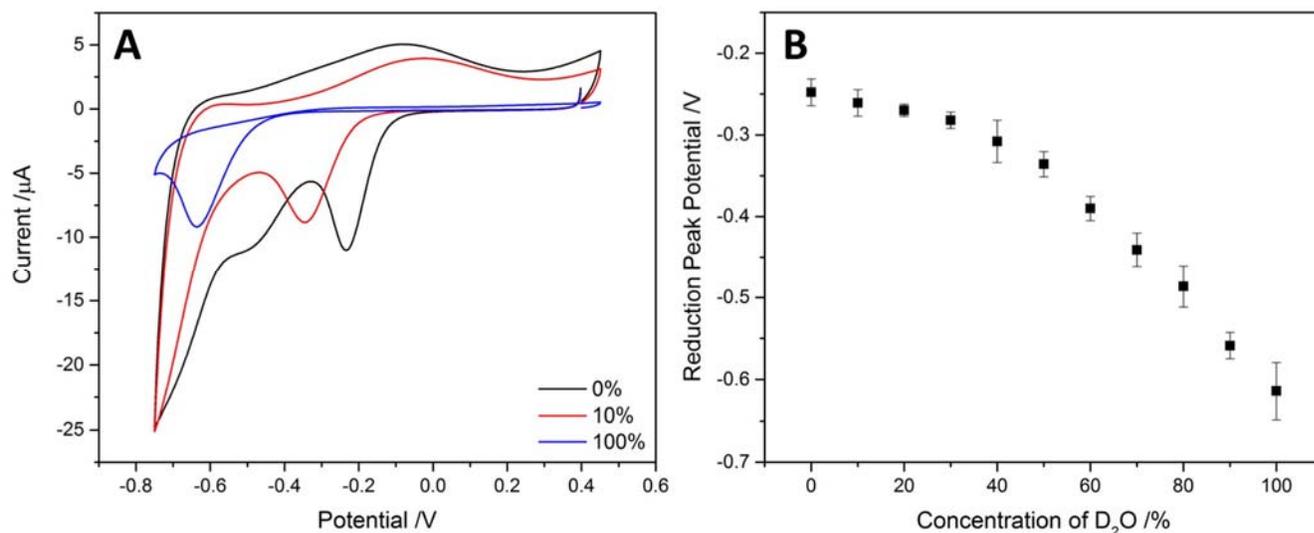
COLL 716

Electrochemistry and viscoelasticity of DNA self-assembled monolayers conjugated with hexamine metal(III) complexes: Effects of H/D isotope exchange

Gerd-Uwe Flechsig, *gflechsig@albany.edu*, **Sarasi K. Galagedera**. *Dept. of Chemistry, University at Albany, SUNY, Albany, New York, United States*

The electroactive complexes hexamine ruthenium(III) (RuHex) and hexamine cobalt(III) (CoHex) form conjugates with DNA self-assembled monolayers (DNA-SAMs) on gold electrodes. We used electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry to investigate how these complexes interact with DNA by formation of hydrogen bonds. Unexpected large frequency changes of more than 20 Hz have been observed when the electrode potential was switched. The frequency changes happened on a millisecond time scale and could not be explained by a mass change due to loss or gain of complex or counter ions, even with consideration of their hydration shells. With 6 MHz resonance frequency, our EQCM sensitivity is relatively low. The observed EQCM response was visible only when a potential jump was applied that

switched the oxidation state of the ruthenium or cobalt central ions, respectively. In case of CoHex, the EQCM frequency shift took considerably longer as compared to RuHex. These findings suggest that the viscoelasticity of the DNA-SAM can be changed when the conjugated metal complexes change their oxidation state. Moreover, CoHex is known to form intermolecular bridges between DNA strands. Indeed, we observed major H/D isotope effects with CoHex in both voltammetric and EQCM studies when we exchanged the solvent by deuterium oxide in the aqueous electrolytes. With RuHex, the H/D isotope effects were significantly smaller. Figure 1 displays the profound H/D isotope effect with DNA-conjugated CoHex in cyclic voltammetry. The D₂O concentration study of the potential shift revealed two linear branches with an intercept at ca. 35% D₂O content. The reduction peak potential was shifted by almost 400 mV (comparing 0 and 100% D₂O). Both redox switching of EQCM response and H/D isotope effects can improve our understanding of the complex behaviour of DNA-SAMs on gold electrodes, because they allow to probe the network of hydrogen bonds.



A) Cyclic voltammetric response of hexamine cobalt(III) conjugated with ssDNA monolayers on gold electrodes at three different D₂O concentrations, B) effect of D₂O concentration on the peak potential of cobalt(III) reduction

COLL 717

Antioxidant hydrogen-bonded films of synthetic polyphenol polymers

Raman Hlushko, raman.hlushko@tamu.edu, Svetlana A. Sukhishvili. Texas A&M University, College Station, Texas, United States

We report hydrogen-bonding driven layer-by-layer assembly of linear antioxidant polymers with a neutral polymer. A family of linear synthetic polyphenols poly(N-(3,4-dihydroxybenzyl) methacrylamide) (P2HMA), poly(N-(3,4-dihydroxy-5-bromobenzyl)

methacrylamide) (PBrHMA), and poly(N-(3,4,5-trihydroxybenzyl) methacrylamide) (P3HMA) were used as hydrogen-bonding donors and poly(ethylene oxide) (PEO) acted as the hydrogen-bonding acceptor. The thickness and composition of the films were monitored by spectroscopic ellipsometry and Fourier transform infrared spectroscopy, respectively. The catechol-based polymers, P2HMA and PBrHMA, exhibited linear growth with thicknesses of 26.2 ± 3.2 nm and 18.3 ± 6.1 nm for 5-bilayer films, respectively. In contrast, gallol containing polymer P3HMA demonstrated exponential growth with a thickness of 88.1 ± 2.8 nm for a 5-bilayer film. These polyphenol LbL films are stable in water up to pH 10 and exhibited high antiradical activity as determined by reduction of 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) radicals. Moreover, these polyphenols demonstrate amphiphilic adsorption abilities to various surfaces while maintaining antioxidant activity. Specifically, these coatings can be deposited onto the intrinsically uneven surface of hydrophobic polyester felt, and decrease its water contact angle value from 120° to 0° .

COLL 718

Influence of molecular weight on assembly and surface properties of polyelectrolyte multilayers

Elizabeth Towle, Ivan Ding, Amy M. Peterson, ampeterson@wpi.edu. Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts, United States

Polyelectrolyte multilayers (PEMs), thin polymer films assembled from polyelectrolytes, are most commonly used as a coating to modify the surface properties of a bulk material, making the optimization of surface properties critical. In this study, the influence of polyelectrolyte molecular weight was examined, as well as the assembly pattern that each molecular weight produces. PEMs were created with poly(acrylic acid) (PAA) and poly-L-lysine (PLL) at low, medium, and high molecular weight to determine the effects of molecular weight on the surface properties of PEMs, specifically surface free energy (SFE) and roughness. Molecular weight has a significant impact on the assembly pattern and therefore the surface properties. Low MW PAA and PLL were found to form less massive PEMs composed primarily of PLL, while high MW PEMs had high mass and more PAA than PLL. Medium MW PEMs had the most linear assembly pattern and were the most balanced between polyelectrolytes. Medium MW PEMs were the smoothest, and had the lowest SFE, while low MW PEMs were the roughest and had the highest SFE. However, high MW PEMs were also quite rough while having a low SFE similar to that of the medium MW PEMs. While further research will be needed to understand how prevalent this specific pattern is with other polyelectrolyte combinations, these results demonstrate the tunability of surface properties including SFE and roughness with molecular weight.

COLL 719

Electrochemically triggered surface deposition of polyelectrolytes

Md Shamim Iqbal¹, *mzi0011@auburn.edu*, **Wei Zhan²**. (1) *Chemistry & Biochemistry, Auburn University, Auburn, Alabama, United States* (2) *Dept. Chemistry, Auburn University, Auburn, Alabama, United States*

An electrochemical approach to surface deposition of polyelectrolytes on self-assembled monolayers is presented. This deposition process can be facilely triggered by a potential bias, which oxidizes ferrocene moieties included in the self-assembled monolayer to ferrocenium, whose charge compensation is provided by the polyelectrolytes and associated counter ions. What makes this approach truly appealing is its generality, which affords quantitative and reproducible deposition of both anionic and cationic polymers covering a wide range of chemical identities (synthetic polymers, peptides and DNA) and molecular weights (10^3 to 10^6 Da). Several techniques, including voltammetry, fluorescence spectroscopy, contact angle analysis, electrochemical Quartz crystal microbalance and atomic force microscopy, were employed to characterize the deposition processes. An electrostatics-based model is proposed to explain the involved deposition mechanisms.

COLL 720

Hybrid glasses coatings obtained by electrospray deposition

Lin Lei¹, *Max Tenorio²*, *Kutaiba Al-Marzoki³*, *Jennifer Guzman⁴*, *Lisa C. Klein¹*, *Assimina Pelegri⁵*, *Jonathan P. Singer⁶*, **Andrei Jitianu⁷**, *andrei.jitianu@lehman.cuny.edu*. (1) *Rutgers University, Piscataway, New Jersey, United States* (4) *City University of New York, Bronx, New York, United States* (7) *Chemistry, Lehman College - City University of New York, Hewitt, New Jersey, United States*

Melting gel (MG) materials are hybrid polysilsesquioxanes that possess glass transition temperatures between -18.8 and 27.7°C and consolidation temperatures at $\sim 150^\circ\text{C}$, above which they irreversibly transform into hybrid-organic inorganic silica based glasses. MGs are synthesized via a sol-gel process involving a monosubstituted alkoxide such as methyltriethoxysilane (MTES) or phenyltriethoxysilane (PhTES) along with a di-substituted alkoxide such as dimethyldiethoxysilane (DMDES) or dipheyldiethoxysilane (DPhDES). In this study two MGs with the following compositions 65%MTES-35%DMDES and 87%PhTES-13%DPhDES were employed. The main advantage of the MGs is their processing ability. MGs can be processed as a thermoplastic melt into a desired form and then converted into a permanent structure based on this property. In our study, melting gel materials are processed by electrospray deposition in order to investigate the kinetic behavior arising from different experimental conditions and how these affect the final morphologies of MG films. Due to the electrostatic breakup mechanism present in electrospray, the resulting sprays possess uniform droplets down to hundreds of nanometers. By using MG dilute loadings of 1 wt%, these microdroplets can deliver extremely small quantities of material at a continuous rate and incorporate fillers to change the properties of the spray and the functionality of the final structures. Control of spray composition, substrate temperature, flow rate, and collection distance, translates to tuning of the dynamic evolution of

solvent evaporation and MG consolidation. The results reveal that these can be used to controllably tune surface structure from dense, to cellular, to superhydrophobic fractal coatings. Nanoindentation tests show that the mechanical properties of the constituent MGs are also affected by these parameters. In addition, manipulation of charge dissipation during the deposition also results in the ability to limit the extent of spray as a means to gain control over the coating thickness.

COLL 721

High yield synthesis of semiconductor helices through self-assembly of CdTe nanoparticles

Jiao Yan^{1,2}, jiaoyan@umich.edu, **Ji-Young Kim**^{2,3}, **Wenchun Feng**⁴, **Nicholas Kotov**¹. (1) *Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States* (2) *Biointerfaces Institute, University of Michigan, Ann Arbor, Michigan, United States* (3) *National Center for Nanoscience and Technology, Beijing, China* (4) *US Food and Drug Administration (FDA), Silver Spring, Maryland, United States*

Chiral helices are the most potential materials for some specific applications, such as chiral catalysis, chiral recognition, negative refractive index materials and optoelectronic devices, etc. Massive efforts have been made to get helices with different materials mostly by physical methods, while work on wet chemistry methods are still less except those with the aid of chiral templates, such as DNA. In this work, by adjusting several parameters, CdTe nanoparticles are able to self assemble into pretty uniform chiral helices with high yield and high reproducibility. The helices show significant chiroptical activity with maximum g factor up to 0.05 in a very broad wavelength range from visible to NIR light. Meanwhile, the strongest chiroptical response range can be modulated easily by changing the pitch of helices. The undermined mechanism to form the helices is suggested that the coordinates made of Cd²⁺ and cysteine mediates the mismatch of CdTe nanocrystal. It is proved that Cd²⁺ and cysteine with a certain ratio would form coordinate at pH around 8, which tends to twist when a poor solvent of cysteine (methanol) was added. It paves a way to construct helical or other structures by modulating the interactions between the interfaces of NPs. Also, it may provide us a sight to understand the origin of chirality in the universe since both metal ions and amino acids are very fundamental and necessary elements to maintain the metabolism of living things. Furthermore, the helices can act as an important candidate for optical modulator due to the excellent capability in tuning the polarization of light.

COLL 722

Universal fluorescence enhancement substrate based on multiple heterostructure colloidal photonic crystal with super-wide stopband and highly sensitive Cr(VI) detecting performance

Lijing Zhang, zhanglj@dlut.edu.cn. *Chemistry, Dalian University of Technology, Dalian, Liaoning Province, China*

Universal fluorescence (FL) enhancement was achieved based on a multiple heterostructure photonic crystal (MHPC). This MHPC film was fabricated by layer-by-layer deposition of annealed colloidal crystal monolayers (CCMs) with gradient sizes, and stopband overlapping and broadening was demonstrated. MHPC with a broadened stopband (from 280 to 650 nm) can overlap with the excitation wavelength (E) and the emission wavelength (F) of most commonly used fluorescent media. More than 100-fold FL enhancement of [Ru(dpp)₃Cl₂], rhodamine 6G (Rh6G) and rhodamine B (RhB) on the MHPC was observed compared to that on a glass substrate. This super-wide stopband MHPC may find significant applications for augmenting FL intensity in chemical and biochemical sensing, imaging, disease diagnosis and environmental monitoring. We further demonstrated the function of MHPC/rhodamine B hydrazide (RBH) composites in the semi-quantitative detection of Cr(VI), and the limit of detection (LOD) of Cr(VI) was effectively improved to 0.2 ppb.

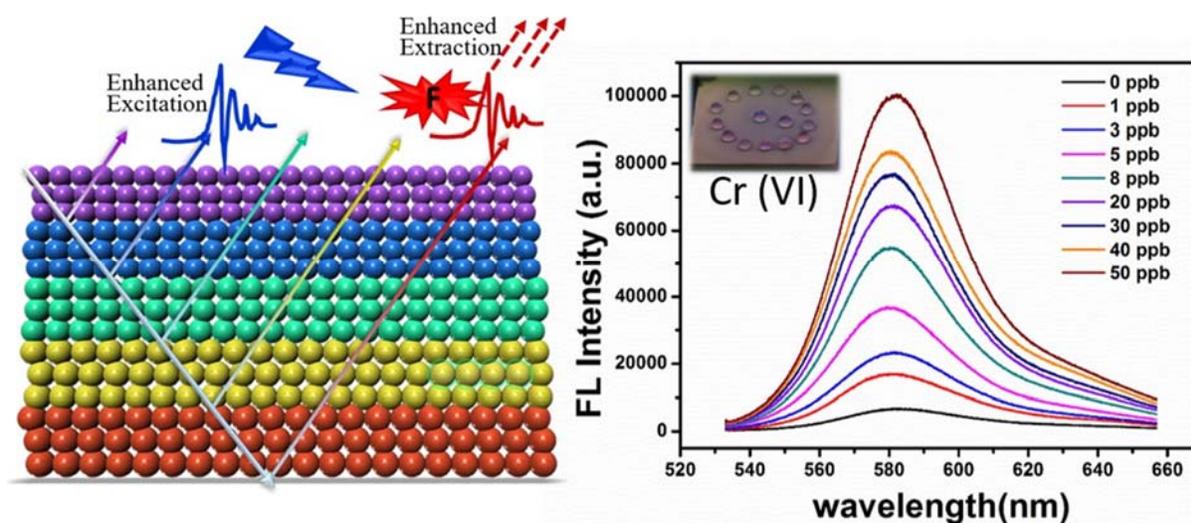


Figure 1. (a) Schematic of the coupling of PC effect and dye molecules in the MHPC structure. (b) The FL spectra of water droplets containing different Cr(VI) concentration based on the MHPC film.

COLL 723

Structural synergy of shell conformation in p-n heterostructured water-processable semiconducting colloids for ultra-fast and long-term quenching efficiency

Yu Jin Kim, yujin.kim@anl.gov. Argonne National Laboratory, Lemont, Illinois, United States

This research describes p-n heterostructured water-borne semiconductor nanoparticles (NPs) with unusual surface structures via a control of shell conformation. The shell particles having n-type semiconductor characteristics notably influence on the

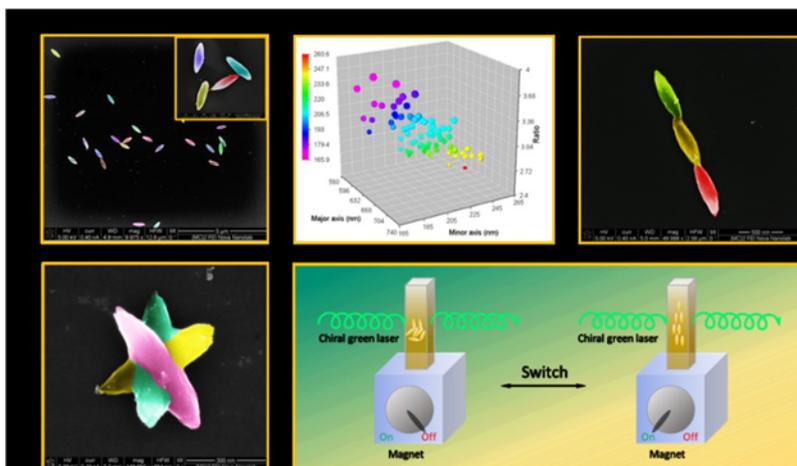
charge carrier behavior in the core-shell structured NPs. The one- or two-phase methodology based on a PC60 surfactant-water and PCBM n-type semiconductor-organic phase provided a highly specific control over the shell structure of the NPs, which allowed their superior charge separation ability. The resulting water-borne NPs thereby showed the shell conformation-dependent carrier quenching effect and stability, which characterized detailed luminescence study. Corresponding to the result, outstanding performances of photovoltaic cells was achieved. The results suggest that the surrounding shell environments, such as the shell conformation, and its electron density, were crucial in determining the overall activity of the core-shell p-n heterostructured NPs. Thus, our research can provide and guide a new protocol in the current fields of water-based organic semiconductor colloids.

COLL 724

Dual self-assembly of chiro-magnetic cobalt-based supraparticles with rice-like structure

Z. Z. Mu^{1,2}, zhengzmu@umich.edu, Nicholas Kotov³. (1) Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States (2) Key Laboratory of Bionic Engineering, Jilin University, Changchun, China (3) Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States

Paramagnetic cobalt oxide (Co₃O₄) nanoparticles (NPs) with chiral distorted crystal lattices were recently discovered exhibiting strong tunable chiroptical activity by magnetic field in visible wavelength range. Although it could provide a versatile experimental system for different fields of science and fundamental problems, ultra-small size (< 5 nm) acts as a hindrance to employ this ceramic NPs in possible magneto- or opto-electronic devices. Herein, we developed a moderate dual assembly method to assemble these Co-based ultra-small NPs into rice-like supraparticles (SPs) expanding their size to hundreds of nanometers (1st order assembly). Moreover, these SPs can spontaneously assemble to form more complex aggregations in intersected or end-to-end ways (2nd order assembly). Interestingly, the strong chiroptical activity of the father NPs was totally inherited by son SPs composed of Co, O, and S. By means of a magnet switch (30 mT), we can easily achieve the goal to adjust the chiroptical activity without disturbing the original dispersions. Further, tunable magnetic field generated by a set of electromagnet could be applied to this system to investigate the inner relationship between the rice-like structure of cobalt-based SPs and corresponding chiroptical activities. It is anticipated to provide additional insight for light-matter effect of circular polarization light and chiral inorganic particles.



COLL 725

Adsorption of rhamnolipid biosurfactant and its effect on the aggregation kinetics of iron oxide (Fe_3O_4) nanoparticles in monovalent and divalent electrolyte solutions

Anushree Ghosh¹, anushree.ghosh@wustl.edu, **Neha Sharma**¹, **Wenlu Li**³, **John Fortner**². (1) Energy Environmental and Chemical Engg., Washington University in St. Louis, St. Louis, Missouri, United States (2) Washington University in St. Louis, Saint Louis, Missouri, United States (3) Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, Saint Louis, Missouri, United States

Rapid expansion of engineered nanomaterial use in commercial products, pharmaceuticals, and cosmetics, among others, warrants better understanding of nanoparticle fate and transport in the aqueous environment. Confounding this reality is the fact that common biological macromolecules, including biopolymers and/or biosurfactants produced by bacteria and fungi – and ubiquitous in the environment, will likely interact with suspended particles. Rhamnolipid biosurfactants, produced extracellularly by *Pseudomonas aeruginosa* are not only widely observed in the environment but are also commercially available for experimental studies. In this presentation, I will describe 8nm iron oxide (Fe_3O_4) nanoparticles with varied surface functional groups and their specific interactions with rhamnolipids through fundamental particle-particle and particle-surface interactions. Specifically, I will quantitatively describe the role of effect of rhamnolipid on particle aggregation processes as a function of pH, ionic strength, and particle surface chemistry. Further, using QCM-D, I will describe the fundamental impact of rhamnolipid on the deposition and release of nanoparticles under the same aqueous matrix. Results from these studies will highlight the crucial role of bio-based surfactants (at low concentrations) with regard to the fate and transport of nanomaterials in the environment.

COLL 726

Developing 3D-printed optical glasses from sol-gel feedstocks

Koroush Sasan¹, sasan2@llnl.gov, **Joel F. Destino**², **Nikola Dudukovic**¹, **Michael A. Johnson**¹, **Du T. Nguyen**¹, **Timothy D. Yee**¹, **Lana L. Wong**¹, **Andrew Lange**¹, **Tyler M. Fears**¹, **Paul Ehrmann**¹, **Rebecca Dylla-Spears**¹. (1) Lawrence Livermore National Laboratory, Livermore, California, United States (2) Department of Chemistry, Creighton University, Omaha, Nebraska, United States

Conventional diffusion-based production methods for gradient-index (GRIN) optics limit their size to few nm in diameter and only allow for monotonic radial gradients. Direct Ink Write (DIW) 3D printing provides a revolutionary approach to design functionally graded materials, including new glass compositions. Herein, GRIN glasses have been prepared from TiO₂-SiO₂ sol-gel colloidal feedstocks by DIW 3D printing. Two inks with different compositions were blended directly in the printing nozzle, then printed into monoliths, dried, and sintered under optimized conditions to ensure complete organic removal and uniform densification, resulting in GRIN glasses. This presentation focuses on the development and characterization of novel, sol-gel derived TiO₂-SiO₂ and GeO₂-SiO₂ inks particle-based formulations for use in DIW inks. Chemical and structural evolution of TiO₂-SiO₂ and GeO₂-SiO₂ glasses were confirmed by several techniques such as X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Fourier transform infrared (FT-IR). Additionally, the role of particle morphology and chemistry are discussed as they relate to the benefits and challenges in preparing the transparent glasses by this method.

COLL 727

Study of the phase state and viscoelastic properties of individual substrate deposited model aerosol systems by atomic force microscopy force spectroscopy

Kamal K. Ray¹, kamalkanti-ray@uiowa.edu, **Hansol Lee**², **Alexei V. Tivanski**². (1) Chemistry, University of Iowa, Iowa City, Iowa, United States (2) Chemistry, The University of Iowa, Iowa City, Iowa, United States

The impact of the aerosols' phase states (liquid, semisolid and solid) on climate is poorly understood. Specifically, aerosols' phase states strongly influences the particles ability to act as a cloud or ice nuclei, and their heterogeneous reactivity. Moreover, aerosols' phase states and viscoelastic properties are interrelated and influenced by the surrounding relative humidity (RH) and hygroscopic nature of the aerosols. However, the interplay of RH dependent viscoelastic properties and corresponding phase state variation of submicrometer sized model aerosols have not been reported yet. Here, we utilize atomic force microscopy (AFM) nanoindentation technique to study the phase states and viscoelastic properties of model aerosols. At first, the nanoindentation methodology was established and applied on individual sucrose particles as a function of RH experimentally determine the phase state transitions from solid to semisolid and from semisolid to liquid state. Specifically, we introduced measurements of viscoelastic response distance (VRD) through AFM force spectroscopy and correlation with aspect ratio (height to area equivalent diameter-AR) of particles. Here, we expanded our study

to more complex, model sea spray aerosol (SSA) and secondary organic aerosol (SOA) systems that include inorganic salts, organic acids, saccharides, and organic-inorganic binary chemical mixtures characterized at fixed ~20% RH. Our results show that both Young's modulus (YM, stiffness), and aspect ratio (AR, ratio of the particle height to area-equivalent diameter) of the particles decrease with increasing VRD. We show how these results can then be used to quantify the solid, semisolid and liquid phase states of particles with unknown composition. Overall, we show here that AFM force spectroscopy and nanoindentation technique can be utilized to quantify viscoelastic properties of substrate-deposited individual particles and identify their physical phase states.

COLL 728

Determination of zeta potential in high ionic strength aqueous colloidal dispersions using next generation electrophoretic light scattering (NG-ELS)

John Miller, john@enlightenscientific.com. Enlighten Scientific LLC, Hillsborough, North Carolina, United States

The ability to measure zeta potential of colloidal particles in high ionic strength aqueous media has growing significant importance in industries that range from large-scale waste water treatment and sea water desalination to small-scale microfluidics. However, current commercial instruments for determining zeta potential, such as electrophoretic light scattering (ELS), do not afford accurate, reliable and meaningful measurement at ionic strengths of the order of 10mM or higher. This oral presentation will describe a next generation ELS technique that permits such measurements to be performed up to ionic strengths of the order of 1M. The underlying limitations of the current generation of ELS instruments will be described. The innovations of the new instrument will be discussed and illustrated with experimental data to show how they can overcome the inherent limitations of current methodology. This new instrument represents the first significant improvement to the ELS method since the invention of phase analysis light scattering (PALS) by the presenter in the late 1980s.

COLL 729

Characterization of fluorocarbon surfactant solutions for understanding fire suppression enhancement with solvent incorporation

Spencer L. Giles, spencer0431@yahoo.com, Arthur Snow, Katherine M. Hinnant, Ramagopal Ananth. Chemistry Division, Naval Research Laboratory, Lorton, Virginia, United States

Fluorocarbon surfactants are currently used in aqueous film forming foam (AFFF) solutions for fighting liquid fuel pool fires. These surfactants display low fuel transport rates through the foam which provides an effective barrier between the liquid pool and the fire above, resulting in rapid extinction. Research into understanding fire

suppression mechanisms with commercial AFFF solutions are hindered due to proprietary formulation with ten or more components. In order to understand the impact of components on fire suppression, two simplistic aqueous solutions containing a single fluorocarbon surfactant concentrate with and without the incorporation of an organic solvent were evaluated for fire suppression. Significant differences in the generated foam and the suppression of a 19 cm diameter heptane pool fire were observed during bench scale suppression testing leading to further investigation into solution properties. Characteristics of the foam solutions were evaluated using dynamic surface tension, dynamic light scattering, and dynamic foam analysis. Solution analysis reveals that the solvent incorporation helps reduce surface tension at a shorter surface age leading to smaller bubble formation during foam generation confirmed through dynamic foam analysis. Dynamic light scattering shows correlating results in that the measured diffusion coefficient of the micelles for the solution containing solvent displayed a higher micelle diffusion coefficient compared to the solution without solvent.

COLL 730

Spectroscopic investigations of AuxPdy bimetallic nanoparticles supported on TiO₂

Xiaojuan Yu, xiaojuan.yu@partner.kit.edu, Alexei Nefedov, Christof Woell, Yuemin Wang. Institute of Functional Interfaces, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Oxide-supported bimetallic AuPd nanoparticles (NPs) are known to exhibit significantly enhanced activity and selectivity in numerous reactions compared to their monometallic counterparts. However, the nature of the improved catalytic performance of alloyed AuPd nanoparticles (NPs) is still under debate. Here we present the results of a thorough study on various monometallic and bimetallic AuxPdy-TiO₂ nanoparticles (x:y = 1:0, 7:3, 1:1, 3:7, 0:1) using primarily ultrahigh vacuum IR spectroscopy (UHV-FTIRS) in conjunction with photoelectron spectroscopy (XPS). The different surface sites of monometallic and bimetallic Au-Pd NPs supported on TiO₂ powders were identified by UHV-FTIRS using CO as a probe molecule. For monometallic Au and Pd NPs, the positively charged Au^{δ+} and Pd²⁺ were detected as majority of species, while for bimetallic AuPd NPs, Au⁰, atop Pd⁰ and bridge Pd⁰ become the dominating species. The strong electronic interaction between Au and Pd in the alloyed AuPd NPs was demonstrated based on the XPS results and the frequency shift of the corresponding CO bands. The catalysis experiments revealed that the Au₃Pd₇-TiO₂ sample exhibits the highest activity for CO oxidation. This was attributed to a synergistic effect where the activation of dioxygen is facilitated at the Pd-enriched sites while both bimetallic Au and Pd sites chemisorb CO.

COLL 731

Layer-by-layer self-assembly of amphiphilic quaternary ammonium chitosans/sodium alginate as a biocompatible anti-biofouling coating

Joonhoo Jung¹, joonhoo_jung@student.uml.edu, Yuyu Sun². (1) Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States (2) Chemistry Department, UMass Lowell, Lowell, Massachusetts, United States

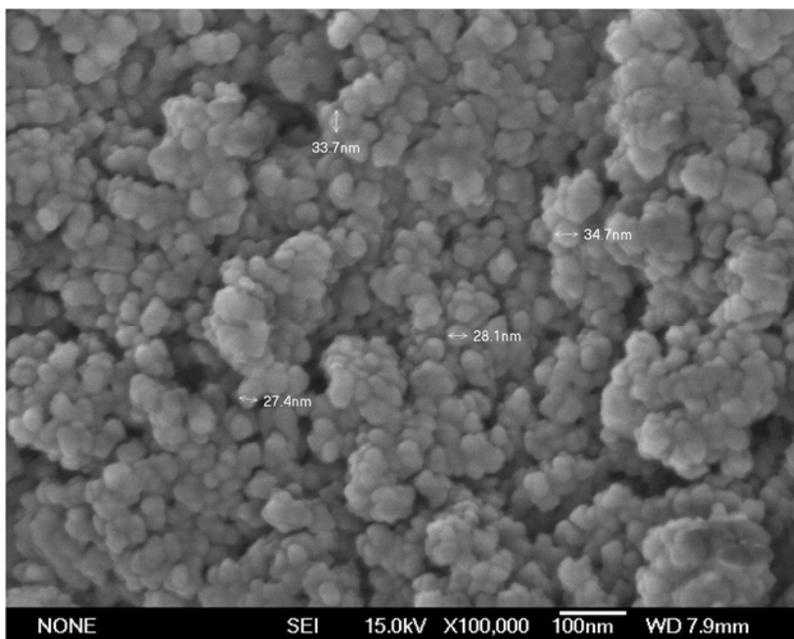
Formation of fungal biofilm on health-related materials is a clinical concern due to a difficulty in removing the biofilm as well as cause of infections. In order to prevent biofilm-related infections, we created a new surface that can prevent the formation of biofilm by layer-by-layer (LBL) technique. LBL self-assembly is a simple and fast technique to engineer surfaces with specific functions. For the one of the layers, we prepare amphiphilic quaternary ammonium chitosans (AQACS) which has an antimicrobial activity as well as a biocompatibility. Sodium alginate (SA) is used as the another layer of LBL multilayers which is an anionic polymer. The AQACS/SA multilayer was formed on poly(methyl methacrylate) (PMMA) substrate via the LBL self-assembly and it is confirmed by measuring surface zeta potential and surface hydrophobicity. The LBL multilayer reduces the fungal initial adhesion and it shows significant decrease in the fungal biofilm formation on the PMMA surface. The hydrophilic bilayers inhibit the microorganism adhesion and the positive charge on the AQACS layer contributes to preventing biofilm formation on the substrate. Furthermore, the AQACS/SA multilayer possesses a durability by showing a good result on repeating test as well as a biocompatibility.

COLL 732

Synthesis and characterisation of silicon germanium oxide ($\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_2$) nanoparticles via liquid mix and sol-gel techniques

Geok B. Teh¹, gbteh@tarc.edu.my, Teck Hock Lim¹, Shangeetha Ganesan², Richard D. Tilley³. (1) Faculty of Applied Sciences, Tunku Abdul Rahman University College, Kuala Lumpur, Malaysia (2) School of Chemical Sciences, Universiti Sains Malaysia, Minden, Penang, Malaysia (3) School of Chemistry, UNSW Sydney, Sydney, New South Wales, Australia

We report here the synthesis and characterisation of nano-sized silicon germanium oxide (SiGeO) nanoparticles with mole ratio of Si:Ge being 1:1 via liquid mix and sol-gel techniques. The SiGeO nanoparticles were characterised via x-ray diffraction, high resolution transmission electron microscopy, field emission scanning electron microscopy and photoluminescence spectrophotometry. The SiGeO nanoparticles were found to have hexagonal crystal system with intense (101) reflections. The morphology studies indicated that the nanoparticles are spherical in shape with diameter ranging from 10 - 35 nm and clustered in nature. Quantitative photoluminescence examination indicated that $\text{Si}_{0.5}\text{Ge}_{0.5}\text{O}_2$ produced via liquid mix technique had significant photoluminescent characteristics with λ_{max} centering at about 430 nm.



SiGeO nanoparticles produced via liquid mix technique

COLL 733

Selective distribution of HOMO-LUMO in gold nanoclusters

Zhikun Wu, zkwu@issp.ac.cn. Institute of Solid State physics, Hefei, China

Both "Highest occupied molecular orbital (HOMO)" and "lowest unoccupied molecular orbital (LUMO)" are important molecular orbitals in molecular orbital theory, and they determine some of the physical and chemical properties of molecular materials, which is also applicable to the metal nanoclusters. Although all of the atoms contribute to the HOMO-LUMO more or less, it is recently found that the major of HOMO-LUMO selectively occupy some positions in metal nanoclusters. In this presentation, we will report some of very recent findings concerning of the selective distribution of HOMO-LUMO in gold nanoclusters. The related electrochemical gaps will also be discussed.

COLL 734

Understanding and prediction of the structures of ligand-protected gold nanoclusters using electron counting rule

Yi Gao¹, gaoyi@sinap.ac.cn, Wenwu Xu¹, Xiao C. Zeng². (1) Shanghai Inst of Applied Physics, Chinese Academy of Science, Shanghai, China (2) Univ of Nebraska, Lincoln, Nebraska, United States

The structures and stabilities of ligand-protected gold clusters have attracted extensive interest in the last decade, although the underlying mechanism has not been well

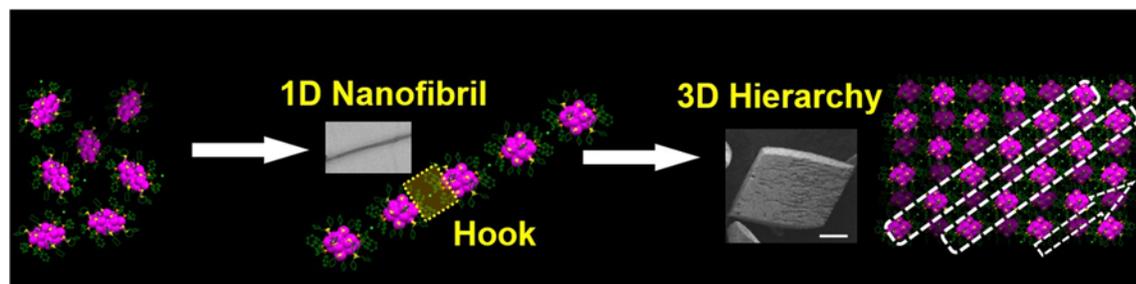
understood by the known Polyhedral Skeleton Electron Pair Theory (PSEPT) or superatom complex concept. Here, we proposed a grand unified model (GUM) to decompose the Au cores of ligand-protected gold nanoclusters to a series of basic units with the high geometrical and electronic stabilities. The basic units (i.e., triangular $\text{Au}_3(2e)$ and tetrahedral $\text{Au}_4(2e)$) can assemble into larger units (i.e. icosahedral $\text{Au}_{13}(8e)$). All the units have closed-shell electron structures (such as 2e and 8e valence electrons), akin to the octet rule in general chemistry. With this model, structures of all published ligand-protected gold clusters in the literature, and their growth mechanism can be deciphered and predicted altogether.

COLL 735

Modulating the hierarchical fibrous assembly of Au nanoparticles with atomic precision

Qi Li, li1@andrew.cmu.edu, Rongchao Jin. Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

The ability to modulate nanoparticle (NP) assemblies with atomic precision is still lacking, which hinders us from creating hierarchical NP organizations with desired properties. In this work, a hierarchical fibrous assembly of Au NPs is realized and further modulated with atomic-precision via site-specific tailoring of a surface “hook” which is composed of four phenyl ligands and an associated counterion. Especially, this fibrous assembly can be exquisitely modulated via tailoring of the associated counterion, which significantly changes the electrical transport properties of the NP-assembled solids by two orders of magnitude. This notable change is primarily due to the altered configuration of the interacting π - π pairs of the surface “hooks”, instead of the commonly invoked factor of interparticle distance. Overall, our success in atomic-level tailoring of the surface “hook” directly evidences how the ligands and associated counterions can function to realize two-dimensional and one-dimensional assembly of NPs and further modulate the one-dimensional assembly of NPs in a delicate manner. The success in atomic-level modulation of the hierarchical NP assembly offers new insight into the structural factors for controlling the electron transport in NP solids. This work expands our skills (e.g. tailoring the counterions) in rationally programming the NP-assembled materials with controllable structures and properties.



COLL 736

Kinetic control of the seed-mediated growth of gold nanorods

Gang Chen, *gang.chen@ucf.edu*, Reese Gallagher, Xing Zhang. Chemistry, University of Central Florida, Orlando, Florida, United States

The research presented here is to understand the synthesis mechanism of gold nanorods (AuNRs) from a kinetic perspective by considering it as a diffusion-controlled reaction, investigate the relationship between the reaction/diffusion speed and the anisotropic growth, and thus optimize the synthesis to improve the shape uniformity and synthesis reproducibility of AuNRs. Although various AuNRs have been produced with different aspect ratio, current synthesis methods through seed-mediated growth are far from ideal, sharing the same drawbacks, such as low yield of gold conversion (~20%), poor shape uniformity and reproducibility, due to a lack of understanding of the reaction mechanism. While the mechanism of the anisotropic growth of AuNRs is not clear yet, the experimental detail in the literatures shows evidence that it is a diffusion-controlled reaction (for example, no stirring, low temperature and reaction rate dependent), where the final products depend on the relative rate of transport of reactants through the reaction medium and the rate of chemical reduction of metal ion. As a diffusion-controlled reaction, both the diffusion rate and reduction rate are important. Basically, the reduction rate depends on both the reactivity and concentration of the reactants (gold salts and ascorbic acid (AA)). The concentration of AA is commonly utilized to control the reduction rate. For example, to decrease the reduction rate, the ratio of AA to gold ion has been optimized to be 1.1 which is far below the stoichiometric ratio (1.5), with extremely poor yield of gold conversion (~20%). To achieve a high gold conversion yield, it is better to keep stoichiometric ratio (1.5) but tuning the reduction rate by reactivity. As a polyol compound, the reactivity of AA depends on the pH of the system. At stoichiometric ratio (1.5), the optimal pH range for AA has been discovered to get perfect AuNRs with improved uniformity, reproducibility and gold conversion yield (> 80%). The gold conversion yield can be improved further at higher ratio of AA to gold ion than the stoichiometry. With the same idea, the PI has extended the reducing agent to other polyol compounds, such as phenol, hydroquinone, catechol, resorcinol, and phloroglucinol. Other kinetic controls were also studied and a model has been created to correlate these factors together.

COLL 737

Hierarchical nanostructures through prescribed structural symmetry breaking

Thomas J. Kempa, *tkempa@jhu.edu*, Benjamin Stephens, Alexander Kossak, Marta Sliwa, Tomojit Chowdhury. Chemistry, Johns Hopkins University, Baltimore, Maryland, United States

Precise control of structural and compositional hierarchy within low-dimensional materials is needed. Hierarchy can be introduced and tuned through prescribed

structural symmetry breaking. First, we discuss the solution-phase synthesis of anisotropic and multi-component nanostructures through photo-stimulation of metal-halide nanoparticles. The complex hierarchical nanostructures are generated at greater than 80% yield, are highly monodisperse, and exhibit crystalline nanophases separated by atomically precise interfaces. We discuss salient mechanistic features of the nanostructure nucleation and growth. Second, we discuss recent results concerning gas-phase synthesis of high aspect ratio 2-dimensional transition metal dichalcogenides (2D-TMD). In-plane growth of the 2D-TMD can be controlled through tailorable interactions with designer substrates. These results point to direct control over the TMD crystal morphology and phase.

COLL 738

DNA-templated silver clusters

Jeffrey T. Petty¹, jeff.petty@furman.edu, Daniel Chevrier⁴, Peng Zhang⁴, Tim Yeh², Robert Dickson³. (1) Chemistry, Furman University, Travelers Rest, South Carolina, United States (2) Biomedical Engineering, University of Texas, Austin, Texas, United States (3) Georgia Inst of Techlgy, Atlanta, Georgia, United States (4) Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

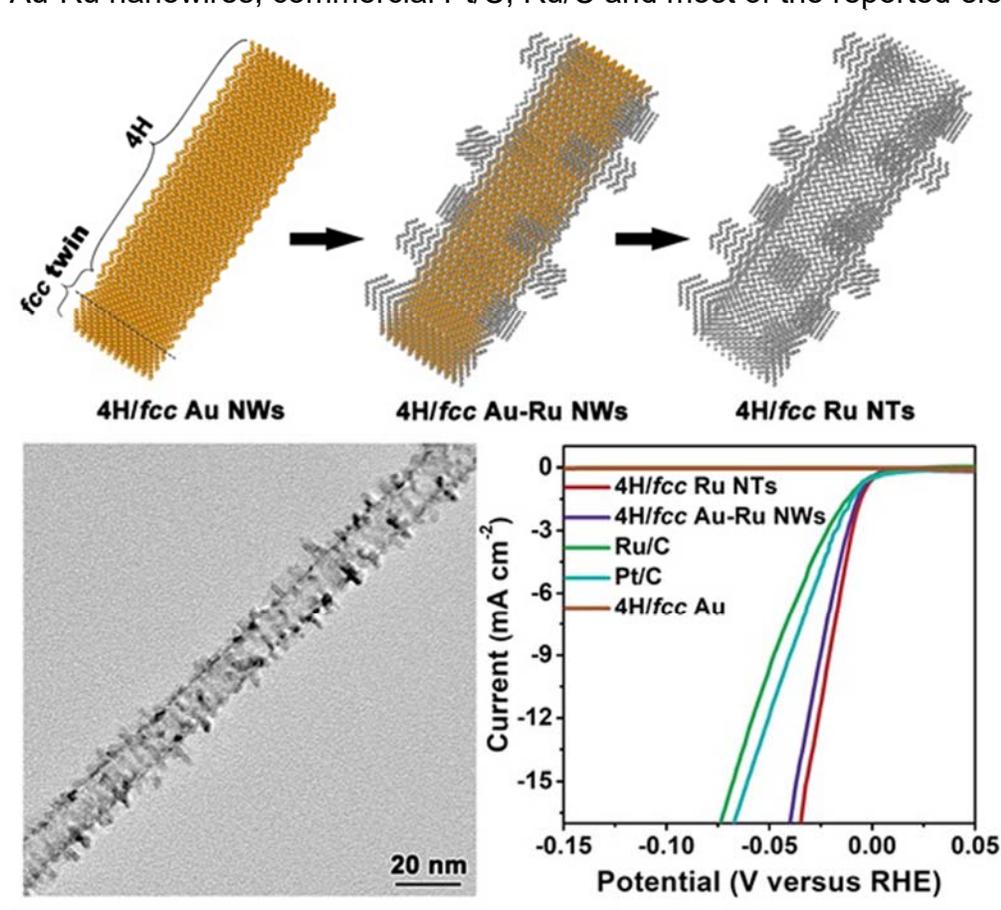
Silver cluster - DNA complexes are optical chromophores, and pairs of these conjugates can be toggled from fluorescently dim to bright states using DNA hybridization. We highlight spectral and structural differences for a specific cluster pairs. We discuss a cluster with low emission and violet absorption that forms a compact structure with single-stranded oligonucleotides and its counterpart with blue absorption and strong green emission. This cluster develops with a single-stranded/duplex DNA construct and is favored by low silver concentrations with $<8 \text{ Ag}^+:\text{DNA}$, an oxygen atmosphere, and neutral pH. The resulting cluster displays key signatures of a molecular metal with well-defined absorption/emission bands at 490/550 nm and with a fluorescence quantum yield of 15% and lifetime of 2.4 ns. The silver cluster is identified as Ag_{10}^{6+} using two modes of mass spectrometry and elemental analysis. Our key finding is that it adopts a low-dimensional shape, as determined from a Ag K-edge extended X-ray absorption fine structure analysis. We discuss recent findings related to the spectra and structure of these complexes.

COLL 739

Synthesis of hierarchical 4H/fcc Ru nanostructures for highly efficient hydrogen evolution in alkaline media

Qinbai Yun, qyun001@e.ntu.edu.sg, Qipeng Lu, An-Liang Wang, Hua Zhang. Department of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore

Crystal phase engineering offers opportunities for the rational design and synthesis of noble metal nanomaterials with unusual crystal phases that normally do not exist in bulk materials. However, it remains a great challenge to synthesize noble heterometallic nanocrystals with novel crystal phases and well-controlled morphologies via wet-chemical synthesis. Here, we use crystal-phase heterostructured 4H/fcc Au nanowires as templates to epitaxially grow Ru nanorods, which preferably grow on the 4H phase and fcc-twin boundary in Au nanowires. After etching the 4H/fcc Au nanowire templates by copper ions (Cu^{2+}) in dimethylformamide, hierarchical 4H/fcc Ru nanotubes can be obtained. The hierarchical 4H/fcc Ru nanotubes contain ultrathin Ru shells (5-9 atomic layers) and Ru nanorods with length of $\sim 4\text{nm}$ and diameter of $\sim 2\text{nm}$ vertically decorated on the surface of Ru shells. As an electrocatalyst for the hydrogen evolution reaction in alkaline media, the hierarchical 4H/fcc Ru nanotubes exhibit excellent electrocatalytic performance with a high exchange current density of 1.81 mA cm^{-2} and a low overpotential of 23 mV at 10 mA cm^{-2} . This performance is superior to the 4H/fcc Au-Ru nanowires, commercial Pt/C, Ru/C and most of the reported electrocatalysts.



COLL 740

Single-walled carbon nanotube mediated *in situ* electrochemistry

Albert T. Liu, t.albert.liu@gmail.com, Yuichiro Kunai, Anton Cottrill, Michael Strano. Chemical Engineering, MIT, Cambridge, Massachusetts, United States

Preparative-scale electrolysis has been used as an industrial process to produce bulk chemicals for more than a century. Yet, examples for electrochemistry in bench-top synthesis and the fine chemicals industry remain scarce, largely due to the lack of access to a standard electrolysis instrument, and, perhaps more importantly, poor reactant-to-electrode transport that fundamentally limits the synthetic through-put. It would therefore be attractive to develop a platform with a tunable voltage supply and a facile integration into high-throughput analytical methods, all the while bypassing the traditional mass transfer limit towards the electrodes. Recent advances in understanding molecular interactions with nanostructured carbon materials have led to a myriad of exotic energy generation schemes. Along with these exciting developments, we have introduced a strategy called asymmetric chemical doping (ACD), which involves a chemical potential gradient established using acetonitrile (CH₃CN) molecular dopants, as a mean of electricity generation. With a tunable voltage output in excess of 1.0 V, and a wide range of compatible solvents including the CH₃CN used in abundance by chemists, we take advantage of this phenomenon, and construct a particulate platform that generates “packets” of electricity on demand, in solution, and drives electrochemical transformations in situ by virtue of interacting with the solvent. We demonstrated the potential to multiplex this form of electricity with high-throughput reaction monitoring, parameter optimization, or even continuous chemical production schemes, into what we have identified as a packed bed electrochemical reactor (PBER). We believe the idea of dividing electricity into modular and customizable units and incorporating them as synthetic building blocks, may address some of the remaining challenges in using preparative-scale electrolysis for molecular assembly.

COLL 741

***In-situ* observation of plasmon-driven hydrogenation reactions within Au@Pd core-shell nanoparticles**

Katherine Sytwu, ksytwu@stanford.edu, *Michal Vadai, Fariah hayee, Ai Leen Koh, Robert Sinclair, Jennifer A. Dionne. Stanford University, Stanford, California, United States*

Surface faceting in nanoparticles can profoundly impact the rate and selectivity of photochemical transformations. However, the precise role of surface termination can be challenging to elucidate since many measurements are performed on ensembles of particles and do not have sufficient spatial resolution to observe reactions at the single and sub-particle level. Here, we investigate plasmon-driven solute intercalation in individual Pd and Au@Pd core-shell nanoparticles with distinct surface terminations. We colloiddally synthesize 40-70nm {100}-terminated Pd cubes, {111}-terminated Pd octahedral, and Au@Pd core-shell nanoparticles, which have enhanced optical response in the visible regime. Using an environmental transmission electron microscope (TEM) coupled with light excitation, we compare the thermodynamics and kinetics of these three geometries with approximately 2nm spatial resolution, and find that they are all similar under dark conditions. Despite their different surface terminations and material compositions, all particle morphologies nucleate the new

phase at the tips of the particle under no illumination. While the hydrogenated phase front must rotate from [111] to [100] to propagate in cubes, the phase front can propagate along the [100], [110], and [111] directions in octahedra. Once the phase front is established, the interface propagates linearly with time and is rate-limited by surface-to-subsurface diffusion and/or atomic rearrangements needed to accommodate lattice strain. Following nucleation, both particle morphologies take similar time to reach equilibrium, hydrogenating at similar pressures and without equilibrium phase coexistence. By varying the illumination wavelength and power, we compare the distinct rates and reaction mechanisms that emerge with and without plasmon excitation. To understand the role of the plasmon, we map out the plasmonic near-field response with 2nm resolution for these hybrid structures, and show how these spatially localized fields affect the photochemistry. Our results highlight the importance of low-coordination number sites, strain, and spatially-localized fields in governing light-driven intercalation reactions.

COLL 742

Investigations of plasmonic enhancement for small molecule oxidation using gold nanoparticle decorated semiconductor heterostructures

Jonathan Boltersdorf, jabolter@ncsu.edu, Gregory Forcherio, Joshua McClure, David Baker, Asher Leff, Cynthia A. Lundgren. U.S. Army Research Laboratory, Columbia, Maryland, United States

Recently, enhanced photocatalytic performance has been achieved by integrating surface plasmon resonant noble metal nanoparticles with traditional metal oxide photocatalysts as a photosensitization strategy to utilize the visible-near infrared solar spectrum for charge carrier generation and photothermal conversion. The application of these hybrid photoreactors is of particular interest for targeting low-temperature plasmonic enhancement aimed at the selective photo-oxidation of aqueous hydrocarbons. Fundamental and experimental investigations on plasmon-mediated photocatalysis, the rational design and synthesis of gold nanoparticle-semiconductor hybrid nanostructured photocatalysts (e.g., AuNP-TiO₂) are probed in this study. The contributions of transverse and longitudinal localized surface plasmon resonance modes were decoupled by irradiating with targeted wavelengths to examine their effects on plasmonically-assisted photocatalytic reactions. The photocatalytic performance was assessed by monitoring the yield of gaseous products during photo-oxidation experiments using a gas chromatography-mass spectrometry-multiple headspace extraction (GC-MS-MHE) analysis method. The sample preparation and reaction conditions are shown to influence the particle characteristics, surface plasmon resonance modes, and product selectivity.

COLL 743

Solvent mixing to induce aggregation: Applications to control molecular motor behavior

Yuchen Wei, *yuchen.wei@rug.nl*, Ben L Feringa. Dept Org Chem, Univ Groningen, Groningen, Netherlands

Light-triggered molecular motors were mainly studied in solutions, revealing that the surrounding environment, i.e. solvent viscosity, could affect the rotary speed. However, natural light-responsive systems, for example, rhodopsin usually function in a more confined environment as in protein. By applying the solvent/non-solvent mixing method to a bulky first-generation molecular motor, we managed to assemble the motors into bowl-shaped aggregates. Varying the ratio of solvent/non-solvent resulted in different extent of confinement inside aggregates, which could further control the motor behavior. To our surprise, while maintaining the photochemical isomerization steps, the thermal helix inversion (THI) was blocked by strong confinement. Furthermore, a backward *trans-cis* isomerization was also observed. Thus, we could control the thermal forward or backward motion of a molecular motor by tuning the solvent/non-solvent ratio.

COLL 744

Molecular dynamics simulations of peptide conformations and interactions with gold nanoparticles

Pavel Rehak, *prehak2@uic.edu*. University of Illinois at Chicago, Chicago, Illinois, United States

Molecular Dynamics simulations were used to study gold nanoparticles (NPs) coupled to heptapeptide crystals, whose structure was determined in the experiments of our collaborators. One crystal had a negligible net dipole moment, while the other had a significant net dipole moment. We examined the stabilization of both crystals, the lifetimes of their peptide components within the crystals, and their interaction with gold nanoparticle. Then, we studied the formation of 20-mer polypeptide fibrils and an attachment of small gold NPs to them. We performed two types of simulations, where 1) individual polypeptides were allowed to diffuse and coalesce into a larger supramolecular structure and 2) a prepared fibril based on NMR data was interacting with a gold NP.

COLL 745

Plasmonic hot-carriers mediated tunable photochemical reactions: A non-adiabatic molecular dynamics study of H₂ splitting

Yu Zhang¹, *zhyhku@gmail.com*, Sergei Tretiak², Tammie Nelson³, Hua Guo⁴, George C. Schatz⁵. (1) Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States (2) Theoretical Div, T-1/CINT, MS B268, Los Alamos Natl Lab, Los Alamos, New Mexico, United States (3) Theoretical Division, Los Alamos National Lab, Los Alamos, New Mexico, United States (4) MSC03 2060, Albuquerque, New

Mexico, United States (5) Chemistry, Northwestern University, Evanston, Illinois, United States

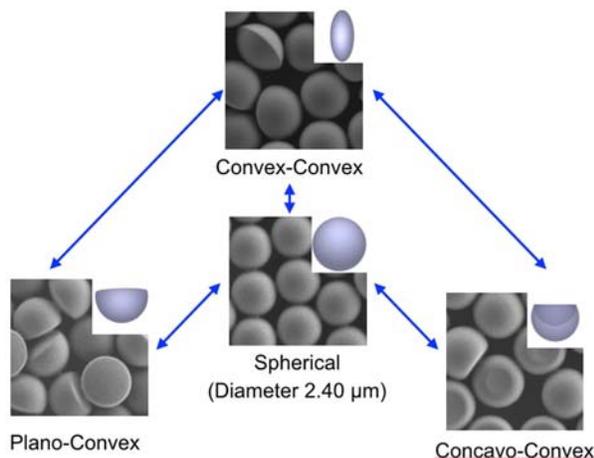
Hot-carrier generation from surface plasmon decay has found many applications in many branches of physics, chemical, materials, and energy science. Especially, recent efforts indicated that the hot-carriers generated from plasmon decay in nanoparticles could transfer to attached molecules and drive the photochemistry of impossible in previous thought. In this work, we explored the atomic-scale mechanism of plasmonic hot-carrier mediated chemical reaction exemplified by H₂ splitting by employing time-dependent density functional calculations theory and non-adiabatic molecular dynamics. The numerical simulation demonstrates that the anti-bonding state of the attached molecule is found to be slightly higher than the Fermi level and the potential energy surface of the excited state of the adsorbed molecule keeps the anti-bonding feature. Consequently, the hot-carriers generated from the nanoparticle can transfer to the anti-bonding state of the attached molecule and drive the photochemical reaction. Then, we also found chemical reaction is tunable if the molecule is placed in the center of the plasmonic dimer. The reaction rate can be either suppressed or enhanced depending on the geometry. In general, symmetry broken is essential to enhance the reaction rate. Thus, our work demonstrates the possibility of tunable photochemistry via plasmonic hot-carriers.

COLL 746

Engineering the shape of non-crosslinked poly(styrene) particles

Mingzhu Liu, ml4885@nyu.edu, Xiaolong Zheng, Fanyuan Dong, Michael D. Ward, Marcus Weck. Chemistry, New York University, New York, New York, United States

A facile and robust method is developed to engineer the shape of non-crosslinked poly(styrene) (Nx-PS) particles. Our strategy allows for the formation of and controlled switching between spherical and three anisotropic morphologies: convex-convex, plano-convex and concavo-convex. The different morphologies are accessible from spherical Nx-PS by modifying the annealing time at elevated temperatures and/or concentrations of surfactant. Furthermore, shape transformations between different morphologies are also achieved. The strategy of engineering the shape of particles might be applied to other polymeric colloids holding great potential in achieving *in situ* colloidal crystal phase transition.



COLL 747

Structure-property relationship in particle brush materials

Jaejun Lee¹, jaejun@cmu.edu, **Zongyu Wang**², **Tingwei Deng**¹, **Robert Davis**¹, **Krzysztof Matyjaszewski**², **Michael R. Bockstaller**¹. (1) Materials science and engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States

Advancement of surface-initiated controlled radical polymerization (SI-CRP) enables coexistence of mechanical robustness and high performance by polymer-grafted nanoparticles, also known as particle brush materials. In this study, how the mechanical properties of particle brushes change with the structure. A variety of particle brushes with systematically controlled density and degree of polymerization of polystyrene (PS) or poly(methyl methacrylate) (PMMA) graft was prepared using surface-initiated atom transfer radical polymerization (SI-ATRP). Evaluation of elastic modulus and fracture toughness were done using nanoindentation and atomic force microscopy on thick assemblies. Particle brush materials with dense and intermediate grafting density exhibit similar structures and trends in the mechanical property. Polymer grafts in the limit of intermediate grafting density were found to be more effective in ‘stiffening’ the particle solid. This effect was attributed to the higher entanglement density of intermediate brush systems. Particles in the sparse analog particularly form string-like connected structures which are attributed to the prevalence of particle surface-surface interactions and become flexible as tethered with longer chains. As a result, the surface graft density is an important parameter governing particle brush architecture and mechanical property. The sparse density materials suggest possible applications for colloidal materials that enable nanocomposite of which the modulus is tunable from ‘hard-sphere-like’ to ‘polymer-like’.

COLL 748

Improvement of personal thermal management by electrically conductive silver nanowire-hydrogel textile coatings

Paola D'Angelo, *paola.a.dangelo.civ@mail.mil*, **Eloizabeth S. Hirst**, *June Lum*. *Biological Sciences and Engineering Team, Natick Soldier Research, Development & Engineering Center, Natick, Massachusetts, United States*

Maintaining comfort levels and protection from arctic cold weather has been an ongoing need in military clothing. Current garment systems are problematic due to overdressing, moisture from sweat, discomfort following strenuous activity, and loss of manual dexterity. These challenges must be balanced in an effort to improve dexterity and mobility while reducing hypothermia and frostbite. Our effort is focused on developing two textile coatings containing silver nanowires (AgNWs) and thermo-responsive hydrogels, which in tandem aim to maintain thermal comfort. AgNWs coatings provide thermal insulation through increased infrared (IR) heat retention as well as active heating due to the conductive properties of the nanowires. The hydrogel coating provides comfort by increasing the textile's wicking capability and reversibly storing moisture. AgNWs were prepared by reducing silver nitrate with ethylene glycol (EG) in the presence of silver seeds and polyvinyl pyrrolidone. AgNW nucleation was assessed through optical microscopy. Fabric of different materials were dip-coated with the nanowire ink and the thermal properties were examined. Scanning electron microscopy and Fourier Transform Infrared Spectroscopy revealed a conductive network of silver nanowires (~105 nm diam.) that were highly thermally insulating with a reflectance of >24% observed for 100% cotton indicating that AgNW-cloth is an effective IR reflector suitable for personal thermal management. Joule heating experiments revealed that the temperature of the AgNW-coated textile could be increased by ~109 °C after applying 3 Volts across the fabric. Thermal images were also investigated and thermal radiation of fabric coated with AgNW ink was decreased by ~3°C resulting in textiles appearing colder. Finally, spacing between AgNWs was determined at ~500 nm suggesting that breathability of the textile was not compromised. Concurrently, efforts are also focused on hydrogel coatings and their behavior after exposure to low temperatures. Three polymer systems –poly (N-isopropylacrylamide), polyethyleneglycol, and poly acrylic acid—were studied for changes in morphology and absorptivity after exposure to – 80 ° C. The gels were able to absorb a significant percentage of water after cold treatment. Further studies aim to optimize coating adherence to textiles and durability. Our developed textile coatings could efficiently provide protection from extreme climatic operating environments.

COLL 749

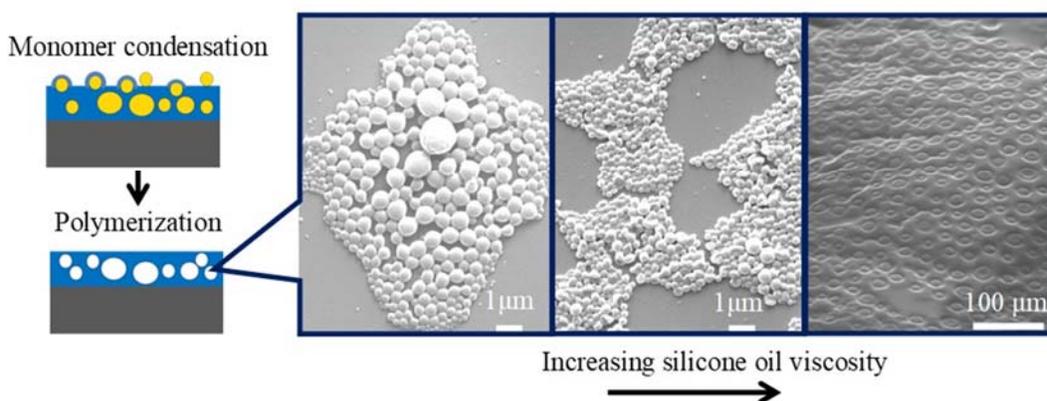
Synthesis of functional particles by condensation and polymerization of monomer droplets in silicone oils

Prathamesh Karandikar¹, *pkarandi@usc.edu*, **Malancha Gupta**². (1) *Chemical Engineering, University of Southern California, Los Angeles, California, United States* (2) *University of Southern California, Los Angeles, California, United States*

The initiated chemical vapor deposition (iCVD) process is an all-dry, vacuum process used to deposit a wide variety of functional polymers. Typically, the monomer and

initiator radicals are introduced simultaneously at process conditions leading to undersaturation of monomer vapors. In this work we report a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism to fabricate polymer particles. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed on 100,000 cSt silicone oil. We studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

Graphical abstract:



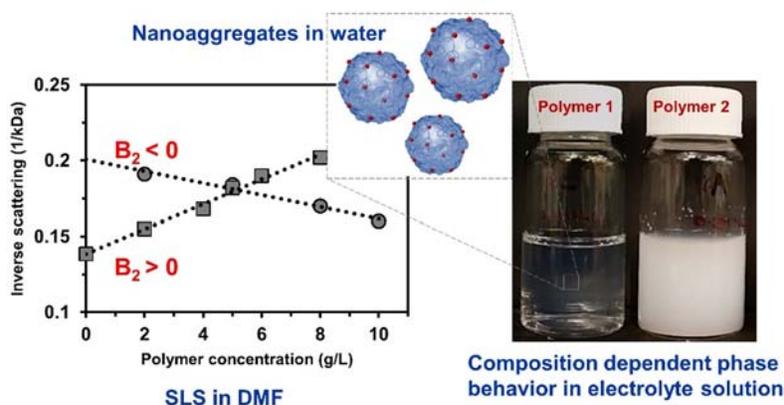
COLL 750

Revisiting the colloidal fundamentals of water-dispersible polyesters: Interactions and self-assembly of polymer nanoaggregates in water

Sabina Islam, sislam3@ncsu.edu, Orlin D. Velev. Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States

Water-dispersible sulfopolyesters are a major class of film-forming and solution-modifying polymers, which are routinely used in applications such as inks, adhesives, coatings, and personal care products. Since these polyesters are designed to be used as waterborne dispersions, understanding their colloidal interactions in dispersions is critical for their application. By using a range of commercially available water-dispersible

sulfopolyesters as a model system, we investigated the relationship between their molecular composition, colloidal interactions, and phase equilibria. We established how these polyesters undergo different molecular configurations and nanoaggregated states, depending on the nature of the liquid medium. For example, the polyesters exist in a solvated molecular form in certain organic solvents, whereas they self-assemble into compact nanoaggregates in water. We found that the interactions of these nanoaggregates follow the classical DLVO theory of critical colloidal coagulation where the stability of these nanoparticles is extremely sensitive to multivalent electrolytes (i.e., $C_{crit} \propto z^{-6}$). By using static, dynamic, and electrophoretic light scattering, we correlate their nanoscale intermolecular and interparticle interactions with the corresponding macroscale phase behavior in both organic medium and water, based on the theoretical framework of second virial coefficients. We present a model for nanoaggregate formation in water based on the critical surface charge density of these nanoparticles. Such fundamental understanding of colloidal interactions could be used to efficiently control and improve the colloidal stability and film-formation ability of these polyesters and may enable the design of novel high-performance surfactant-free waterborne dispersion systems.



When suspended in water, polyester ionomers self-assemble into soft nanoaggregates, whose colloidal properties can be predicted by classical DLVO theory.

COLL 751

Green synthesis of polyrhodanine microspheres and its application for the adsorption of organic dye

Moni Chauhan¹, mchauhan@qcc.cuny.edu, **Anjali Gaba**¹, **Yousif Saleh**¹, **Qiaxian R. Johnson**², **Gurjeet Longia**², **Bhanu P. Chauhan**³. (1) Chemistry, Queensborough Community College of CUNY, Staten Island, New York, United States (2) William Paterson University, Jackson, New Jersey, United States (3) Department of Chemistry, William Paterson University, Wayne, New Jersey, United States

Rhodanine (Rh) and its derivatives have immense antibacterial, antiviral, antihistaminic, and anticorrosion properties. High-quality polyrhodanine (pRh) films prepared

electrochemically and silver/pRh nanotubes and nanofibers composite materials synthesized via chemical oxidative polymerization exhibits immense antimicrobial efficacy against Gram-negative, Gram-positive bacteria and yeast. pRh polymer similar to polypyrrole, polyaniline, and polythiophene are very useful materials for micro sensors, high environmental stability, and catalysis attributed to pi-electron delocalization. Recently, hollow polymeric composite materials have triggered great interest in the area of material science due to their large surface area, alterable particle diameter, shell thickness, low permeability, and density. To our knowledge, there is no report for the direct one-pot green synthesis of pRh nano spheres either with or without using a template. Since pRh has coordination sites N, O and S with lone pair of electrons, it is known to complex with heavy metals and remove them from aqueous solutions. These nanospheres have a positive charge localized over its backbone and hence make it an ideal candidate for the removal of anionic dye (Methyl Orange) from the wastewater. This presentation will cover microwave synthesis of metal catalyzed pRh micro spheres and its characterization via SEM, TEM, FT-IR, UV-vis, and Raman Spectroscopy. Kinetic study of Methyl Orange adsorption by Polyrhodanine nanospheres will also be discussed.

COLL 752

Soft-templating of ultra-large pores using block bottlebrush copolymer via a cooperative assembly approach

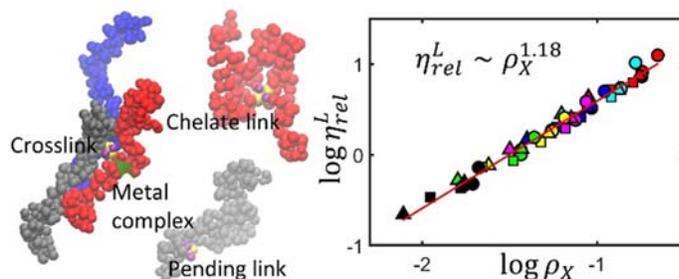
Xuhui Xia¹, xx14@zips.uakron.edu, Garrett Bass², Matthew Becker³, Bryan D. Vogt³. (1) Polymer Engineering, University of Akron, Akron, Ohio, United States (2) Polymer Science, University of Akron, Akron, Ohio, United States (3) University of Akron, Akron, Ohio, United States

Porous metal oxides are enabling materials for a wide range of applications. Much work has focused on the cooperative assembly of precursors with block copolymers to synthesize a wide variety of metal oxides, but sizes of the pores are generally mesoporous due to the scaling of template dimensions with molecular weight ($N^{1/2}$). In this work, we demonstrate a route to overcome this intrinsic limitation for block copolymer templates through the use of block bottlebrush copolymers. A generalizable approach to macroporous metal oxide films is demonstrated through the cooperative assembly of metal nitrates, citric acid, and a norbornene-based block bottlebrush copolymer containing poly(ethylene oxide) and poly(t-butyl acrylate) side chains. After calcination, ellipsoidal pores (~200 nm in long axis) are generated even when the framework is highly crystalline. Interestingly, the porosity of these metal oxide films reaches as high as ~65%, which is double the maximum porosity achieved in analogous porous films templated by linear block copolymers with similar polymer chemistry. Additionally, the spectrum from evaporation induced self-assembly (EISA) to persistent micelle templating is probed using mixed solvents to determine the impact of the solvent selectivity on the porous metal oxide morphology (size, porosity, and structure). Insights into how to control structure and properties of macroporous films templated by block bottlebrush copolymers will be discussed.

Elucidating the effects of metal-complexation on morphological and rheological properties of polymer solutions by a dissipative particle dynamics model

Aleksey Vishnyakov, shibboleth@list.ru, Santo Kolattukudy Poulouse, Alexander V. Neimark. Chemical & Biochemical Engineering, Rutgers the State University of NJ, North Brunswick, New Jersey, United States

When a salt is added to a polymer solution, metal cations may coordinate with polymer ligands forming interchain and intrachain links. Metal coordination leads to drastic changes of polymer morphology, formation of clusters and, ultimately, to sol-gel transition that affect the solution rheology. We propose a coarse-grained dissipative particle dynamics (DPD) model to study morphological and rheological properties of concentrated solutions of polymers in the presence of multivalent cations that can coordinate the polymer ligands. The coordinating metal is introduced as a 3D complex of pre-selected geometry with the central DPD bead representing the metal cation surrounded at the vertices by dummy beads representing coordination sites some of which are occupied by counter-ions. Coordination is modeled as the dynamic formation and dissociation of a reversible link between the vacant coordination site and a ligand described by the Morse potential. The proposed model is applied to study the specifics of the equilibrium morphology and shearing flow in polyvinyl pyrrolidone - dimethylformamide solutions in the presence of metal chlorides. Coordination leads to interchain and intrachain crosslinks as well as to metal cations grafted onto polymer chains by a single link. The interchain crosslinks induce a sol-gel transition to a weak gel phase as the metal concentration increases. Due to the reversible nature of interchain crosslinks, the weak gel phase behaves as a viscoelastic fluid, the viscosity of which gradually increases with the metal concentration and decreases as the shear rate increases. The change of viscosity due to interchain coordination crosslinks scales with the interchain crosslink density and the metal concentration according to the power law with the exponent. The simulation results are in qualitative agreement with available literature data. The proposed DPD model provides a physical insight into the morphological features of polymer solutions in the presence of multivalent salts and can be extended to other coordinating systems such as metal-substituted polyelectrolytes.



COLL 754

Impact of amine rich polyelectrolyte coating chain length on AuNP-Liposome interaction

Zheng Zheng, zz1@umbc.edu, Zeev Rosenzweig. Chemistry, UMBC, Catonsville, Maryland, United States

The length of polyelectrolyte used to coat nanoparticles can greatly impact its behavior on a nanoparticle's surface. This in turn affects the behavior of nanoparticle-membrane interactions. Amine rich polyelectrolyte coatings have been shown to have significant intramolecular and intermolecular interactions between amine on the same and neighboring chains, respectively. The length of the polyelectrolyte coating impacts the degree of these interactions and affects coating density, particle stability, and membrane association. We synthesize AuNPs coated with 16-20 KD poly-oxanorboronenes of varying amine content to determine their membrane impact on model liposomes mimicking bacterial and mammalian membranes. Significantly different behavior is found compared to previous experiments conducted with 3KD poly-oxanorboronenes with similar amine content.

COLL 755

Comparison of structure-property relationship of molecular gels prepared from simply structured alkanolic acid derivatives as efficient ambidextrous gelators

Ajay V. Mallia, amallia@ggc.edu, Katelyn Galinat, Cassandra Dill. School of Science and Technology, Georgia Gwinnett College, Lawrenceville, Georgia, United States

Molecular gels are viscoelastic soft materials composed of a small concentration of a low molecular mass compound (gelator) and a liquid. The gelator molecule aggregate via weak intermolecular interactions changing from 0-dimensional sol/solution to 3-dimensional self-assembled fibrillar networks. Simply structured molecules are very important to understand the gel formation mechanism to know why molecules self-assemble at different distance scales. In this presentation, we systematically compare the structure-property relationship of simply structured fatty acid derivatives (ammonium, sodium, copper (II), nickel (II), cobalt (II), iron (III) salts and N-phenyloctadecanamide derivatives). Correlations between the molecular structures of the gelators and the properties of their gels, including critical gelator concentrations, periods of stability, and gel-sol transition temperatures, thermodynamic, spectroscopic and rheological properties will be presented. Many of the examined gels recover their viscoelasticity after being destroyed by high strain. Polarizing microscopic studies show that the self-assembled fibrillar networks of the gels consist of spherulitic crystalline objects.

COLL 756

Dynamics and mechanism of polyelectrolyte-neutral block copolymer micellization in aqueous solution by explicit atomistic MD simulations

Rajalakshmi Chockalingam, Upendra Natarajan, unatarajan@iitm.ac.in. Department of Chemical Engineering, Indian Institute of Technology (IIT), Chennai, India

The micellization kinetics, dynamics and diffusional properties of asymmetric and symmetric poly(styrene)-*block*-poly(acrylic-acid) polyelectrolyte-neutral block copolymer chains in salt-free aqueous solution were investigated as a function of the copolymer composition (X_{PS}) for un-ionized (acidic, $f = 0$) and ionized (charged, $f = 1$) PAA block by molecular dynamics simulations. This is the first such study on the aggregation of synthetic polyelectrolyte block copolymer in aqueous solution carried out by atomistic MD simulation in explicit solvent. The mechanism of the formation of the micelle was tracked using the population of unimer and clusters across the simulation trajectory, which confirmed that the asymmetric copolymer micelle follows a combined approach of unimer insertion and cluster fusion mechanism, while the symmetric micelle follows unimer insertion method exclusively. Micelle formation takes a longer time for copolymers having charged (ionized) PAA block ($f > 0$) and relatively short PS block ($X_{PS} < 0.5$) due to the presence of a greater number of hydrophobic groups, which is in qualitative agreement with observations of the DPD simulation study on model copolymer micelles available in literature. Conformational dynamics studied using relaxation of backbone dihedral angle and radius-of-gyration, specifically for core and corona blocks, shows a slower relaxation of the hydrophobic insoluble PS blocks as compared to the soluble PAA blocks. With respect to the fraction of the PS block (X_{PS}) the conformational relaxation time increases linearly for PS and is invariant for PAA. The interaction dynamics of PS-*b*-PAA copolymer micelles studied via the relaxation times of PAA-PAA inter-chain hydrogen bonds ($T_{HB,PP}$) and PAA-water inter-molecular hydrogen bonds ($T_{HB,PW}$) show an increase of $T_{HB,PP}$ and a decrease of $T_{HB,PW}$, with increase in X_{PS} . The relaxation of PAA-water h-bonds is slower at $f = 1$ than at $f = 0$, due to the stronger affinity of ionized PAA units to water molecules. The diffusivity of the micelle cluster decreases exponentially with increase in X_{PS} , which is in agreement with results in the literature available for coarse-grained and DPD simulations of model star polymer and copolymer micelles, as well as PFG-NMR measurements of PEO-*b*-PCL and POE-*b*-PDMS micelles in water.

COLL 757

Layer-by-layer growth of DNA-functionalized nanoparticle thin films with tailored surface architectures

Diana Lewis¹, djlewis@mit.edu, Paul Gabrys², Robert Macfarlane². (1) Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

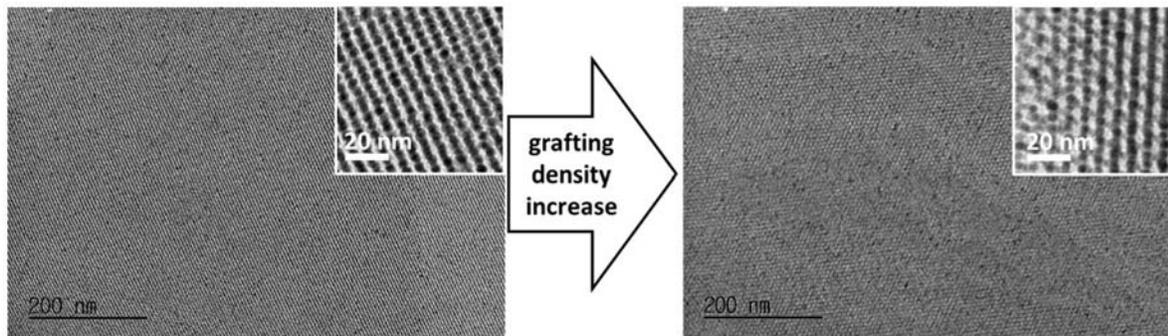
DNA-functionalization can uniquely tune the architecture of deposited nanoparticle thin films through independently modifying the strength of the nanoparticle-surface interaction and the interparticle repulsion by altering the DNA binding sequence and ionic strength of the solution. In addition, due to the weak polyvalent binding, the DNA-nanoparticle system exhibits surface diffusion and rearrangement that allows for tuning of the morphology through modification of the deposition temperature. The programmability of the DNA-nanoparticle system leads to precise control over the morphology of monolayers, as well as the ability to generate crystalline materials with controllable surface roughness, grain size and crystallographic symmetry through layer-by-layer growth. The increased control over thin film morphology allows for the measurement and tailoring of the mechanical properties of these systems, and holds promise for their use in a variety of applications.

COLL 758

Self assembly of polymer coated Au nanocrystals with controlled polymer grafting density

Hongseok Yun¹, hongsyun@kaist.ac.kr, Youngjun Lee¹, Jin-Seong Kim¹, Junghun Han¹, Gila Stein², Bumjoon Kim³. (1) Chemical and Biomolecular Engineering, KAIST, Daejeon, Korea (the Republic of) (2) University of Tennessee, Knoxville, Tennessee, United States (3) KAIST, Daejeon, Korea (the Republic of)

Colloidal nanocrystals (NCs) can serve as promising building blocks for the development of metamaterials. NCs show novel optical, magnetic, and catalytic properties that are not found in nature, not only by modifying surface-to-volume ratio, particle-to-particle distance, and chemical composition, but also by changing assembly structures, which stresses the importance of developing strategies that can precisely control NC assembly structures. Herein, we present preparation of polystyrene coated gold NCs (Au@PS) and manipulation of their assembly structures through PS grafting density control. As-prepared Au@PS particles with different grafting densities were self-assembled through liquid-air interface self-assembly technique which allowed formation of large area NC superlattices. The 3-dimensional structures of Au@PS with different PS grafting density were investigated using transmission electron microscope (TEM) and grazing incidence small angle x-ray scattering (GISAXS) measurements. Interestingly, we observed the structural transition from non-close packed structure (i.e., body centered cubic structure) to close packed structure (i.e., face centered cubic or hexagonal close packed structure) when increasing grafting density, which can be attributed to the transition of the polymer shell from soft shell to hard shell upon grafting density increase. We believe this work paves a new way to manipulate NC assembly structure for building new metamaterials.



TEM images of Au@PS assembly structure at low (left) and high (right) grafting density

COLL 759

Multiscale modeling of DNA-wrapped carbon nanotube nanosensors

Lela Vukovic, *lvukovic@utep.edu*, *Aliasghar Alizadehmojarad*. *Chemistry and Biochemistry, University of Texas at El Paso, El Paso, Texas, United States*

Molecular nanosensors can be used for sensing of minute concentrations and spatial distributions of neurotransmitter molecules released by neuron cells. Here, we present our classical, quantum and analytical modeling of single stranded (ss) DNA-carbon nanotube (CNT) conjugates, used as optical sensors of neurotransmitters. We have performed multiscale simulations of the DNA-(GT) n -(9,4)CNT complexes to disclose mechanisms responsible for varying fluorescence (sensing) responses of the systems examined in experiments of our collaborators. Our studies show that variations in polynucleotide length and the presence of the neurotransmitter molecules can lead to large changes in the conformational stability of the polynucleotide CNT wrapping and CNT fluorescence. We propose a novel mechanism of the CNT fluorescence change within DNA-(GT) n -CNT conjugates, originating in modulations of the electrostatic environment of the exciton.

COLL 760

Hybrid conjugated oligomer/polymer-metal nanoparticles

Donus Tuncel^{1,2}, *dtuncel@fen.bilkent.edu.tr*. (1) *Chemistry Department, Bilkent University, Ankara, Turkey* (2) *UNAM- National Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkey*

Hybrid organic-inorganic nanostructures containing metals (e.g., Ag and Au) and polymers are very intriguing materials, as they combine the flexible and tailorable features of polymers with optical, electrical, and photophysical properties of metals, and because of these synergistic properties, they can find applications in areas including catalysis, plasmonic lasers, sensing, and theranostics.

We combine intrinsically fluorescent conjugated oligomers/polymers with Au or Ag nanoparticles in one platform to be used as a multimodal therapeutic nanocarrier in which due to gold, photothermal therapy and the conjugated oligomer/polymer matrix photodynamic therapy would be possible. Moreover, nanoparticles could also be loaded with drug molecules for the additional chemotherapeutic effect. Imaging would also be possible due to the inherent luminescence properties of the matrix.

In our design for the formation of metal nanoparticles, there is no need to use of extra reducing agents as the oligomer or polymer used acts a matrix to accommodate the metal ions as well as has ability to reduce the ions and form nanoparticles. Depending on the design we select, it would be possible to obtain raspberry type hybrid nanoparticles in which metal particles grow on the surfaces of the nanoparticles or core-shell type hybrid nanoparticles in that the metal ions are entrapped by the nanoparticles and subsequently reduced into their metallic state and allow the formation of core metal nanoparticles.

Additionally, we are also working on the encapsulation of super paramagnetic iron oxide nanoparticle (SPIONs) by conjugated oligomers/polymers for dual optical and magnetic imaging applications. In this approach, conjugated polymers with cross-linkable groups are used in order to hold tightly the SPIONs and prevent their leakage. These hybrid nanoparticles could also be loaded with drug molecules for the extra chemotherapeutic effect.

COLL 761

Directed organization of giant quantum dots (gQDs) during polymerization of ionic liquid (IL) crystalline mesophases

Amrita Joshi¹, amitaj86@gmail.com, Harsha Magurudeniya¹, Christina J. Hanson¹, Jennifer A. Hollingsworth³, Millicent A. Firestone². (1) MPA-CINT, Los Alamos National Lab, Los Alamos, New Mexico, United States (2) Materials Physics & Applications, Los Alamos National Laboratory, Santa Fe, New Mexico, United States (3) Los Alamos National Laboratory, Los Alamos, New Mexico, United States

Formation of hierarchical nanocomposite, constituting of different components can lead to the understanding of integration of individual properties and emergence of new that come into play from the interaction between the components. Incorporation of nanomaterials into ordered polymer matrices has attracted interest, offering the possibility to create multi-functional hybrid materials combining the attributes of polymers with the opto-electronic properties of nanomaterials. Several recent reports have detailed the mixing or formation of nanocrystals within polymeric materials as a means to create composites that have the additive value of the individual components. By designing nanocomposite from the solvent responsive polymer matrices with embedded inorganic nanocrystals that are stable emitters, we can study the complex interplay of these properties in a nanocomposite and we can modulate precisely the particle packing and arrangement for functional modulation. Externally synthesized

quantum dots (QDs) were introduced into the ionic liquid monomer conjugate. Specifically, the bromodecylthiol ligand was synthesized and attached to the QD surface by ligand exchange process and then was conjugated to 3-decyl-1-vinylimidazolium chloride $[C_{10}VIm^+][Cl^-]$ ionic liquid monomer to further self-organize into highly structured lyotropic amphiphilic ionic liquid-QD conjugate mesophases through control of different water compositions, and captured into durable nanostructures by polymerization. Ionic liquid monomer and QD samples were synthesized separately. CdSe/CdS and PbS/CdS core-shell type QDs with vinylimidazolium monomer were conjugated onto 3-decyl-1-vinylimidazolium chloride ionic liquid monomer to construct the ionic liquid-QD conjugate monomer. The pre-formed mesophase polymerized using UV initiated free radical polymer ionic liquid-QD nanocomposite. The work paves the way to a facile, inexpensive path forward to overcome limitations in harnessing the properties of multiple functional nano-components and will serve as an ideal material for efforts producing a multi-scale and multi-dimensional assembly of nanoscale building blocks and will lead to a composite displaying emergent photonic properties such as super-radiance or lasing.

COLL 762

Open circuit chemical corrosion drives porosity evolution of 3D bicontinuous nanoporous precious metal structures: *In situ* and real time kinetic study via synchrotron small angle X-ray scattering

Ahmed A. Farghaly¹, abozeedfaraa@vcu.edu, Maryanne M. Collinson², Byeongdu Lee¹, Soenke Seifert¹, Kamlesh Suthar¹. (1) Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois, United States (2) Chemistry, Virginia Commonwealth University, Richmond, Virginia, United States

Recent advancement in the nanotechnology has led to a tremendous interest in 3D bicontinuous nanoporous precious metal structures due to their wide range of technological applications in nanobonding, catalysis, sensing, biotechnology, drug delivery, separation science, filtrations systems, energy storage, X-ray optics, accelerator components, etc. This study investigates the mechanism of formation of these unique nanostructures from binary/ternary metal alloys using *in situ* small angle X-ray scattering (SAXS). Kinetics of porosity evolution in 3D bicontinuous nanoporous precious metal structures have been studied and real time SAXS data was collected at the Advanced Photon Source using the X-ray beam line at sector 12-ID-C. The nanoporous structures are produced by the selective dissolution of the less noble component of a binary/ternary metal alloy in nitric acid.

Morphological examination of the evolving structures shows the presence of relatively large sized cylindrical pores ~ 80 nm within the bicontinuous nanoporous metal framework. This finding reflects the hierarchical porosity of the evolving bicontinuous structure.

The effect of nitric acid concentration on the porosity evolution kinetics and final morphology of the nanoporous framework has been studied. The SAXS and scanning

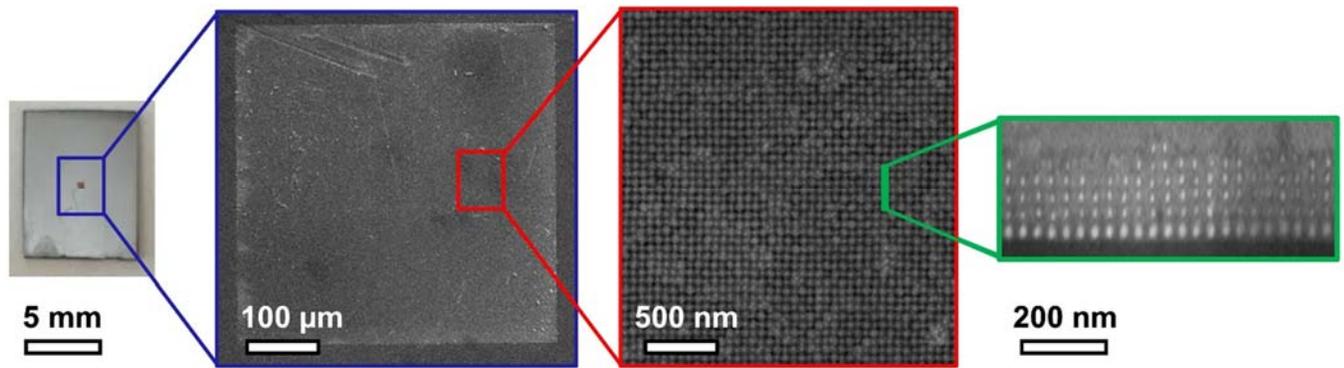
electron microscopy (SEM) results indicated that density of the cylindrical nanopores is inversely proportional to the nitric acid concentration.

COLL 763

"Soft" epitaxy in DNA-nanoparticle thin films

Paul Gabrys, pgabrys@mit.edu, Robert Macfarlane. Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices in a manner that mimics many aspects of atomic crystallization. However, the synthesis of multilayer single crystals of defined size remains a challenge. Here, a comprehensive approach is taken to study fundamental elements, such as the growth temperature and the thermodynamics of interfacial energetics, to achieve epitaxial growth of nanoparticle thin films. Both surface morphology and internal thin film structure are examined to provide an understanding of particle attachment and reorganization during growth. Under equilibrium conditions, single crystalline, multilayer thin films can be synthesized over $500 \times 500 \mu\text{m}^2$ areas on lithographically patterned templates, whereas deposition under kinetic conditions leads to the rapid growth of glassy films. Importantly, these superlattices follow similar patterns of crystal growth demonstrated in atomic thin film deposition, but utilize a "soft," elastically malleable building block. This key difference results in these colloidal thin films exhibiting significant strain tolerance when subjected to heteroepitaxial growth with a lattice mismatch. Calculations of interaction potentials, small-angle X-ray scattering data, and electron microscopy images show that the oligomer corona surrounding a particle core can deform and rearrange to store elastic strain up to $\pm 7.7\%$ lattice mismatch, substantially exceeding the $\pm 1\%$ mismatch tolerated by atomic thin films. Importantly, these DNA-coated particles dissipate strain both elastically through a gradual and coherent relaxation/broadening of the mismatched lattice parameter and plastically (irreversibly) through the formation of dislocations or vacancies. These data also suggest that the DNA cannot be extended as readily as compressed, and thus the thin films exhibit distinctly different relaxation behavior in the positive and negative lattice mismatch regimes. These observations provide a more general understanding of how utilizing rigid building blocks coated with compressible polymeric materials can be used to control nano- and microstructure through "soft heteroepitaxy."



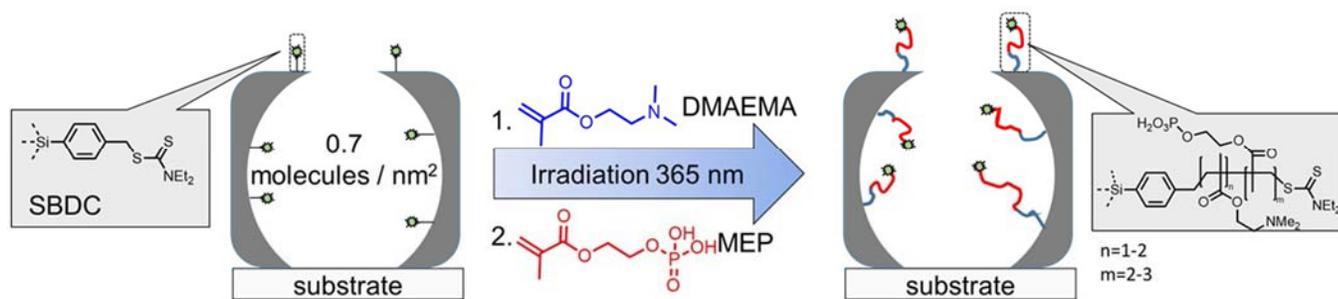
COLL 764

Influence of chain architecture on transport properties in polyelectrolyte functionalized mesopores

Robert Brilmayer, brilmayer@cellulose.tu-darmstadt.de, **Annette Andrieu-Brunsen**. *Technical University Darmstadt, Darmstadt, Deutschland, Germany*

Controlling nanoscale structure and function is highly important for the fabrication of functional materials which are used, for example, in sensing, separation, or drug delivery. Whereas the structure of nanopores and -channels can be well controlled through self-assembly or track etching processes, the controlled functionalization remains a challenge. In recent years it has been demonstrated that photoiniferter initiated polymerization (PIP) offer the possibility to adjust the polymer amount and with this ionic permselectivity in mesoporous membranes. Based on results on zwitterionic polymers rendering mesopores bipolar and thus inaccessible to ions and calculations on charge transitions of poly(2-(methacryloyloxy)ethyl-phosphat (PMEP) in spatially confined pores, the question about the polymer chain architecture influence on mesopore performance attracted our interest. In this frame we present results on the functionalization of silica mesopores with block-co-oligomers using PIP (Fig. 1). Suitable candidates of interest to modulate charge density in mesoporous polymerhybrid films and thus to control their ionic permselectivity is the polyacid PMEP as well as the 2-dimethylaminoethylmethacrylat (DMAEMA)-co-MEP block copolymer. In contrast to solution but in accordance to molecular theory we only observe one pK_s value for PMEP confined into mesopores. In addition, chains in a block like architecture induce a different pH-responsive mesopore accessibility as compared to zwitterionic polymers. Results on ionic permselectivity are obtained by cyclic voltammetry for mesoporous films of varying pore sizes in dependence of solution pH. We currently work on comparing those results with spectroscopic investigations of “pH” in spatially confined

mesopores using pH-responsive fluorescence dyes.

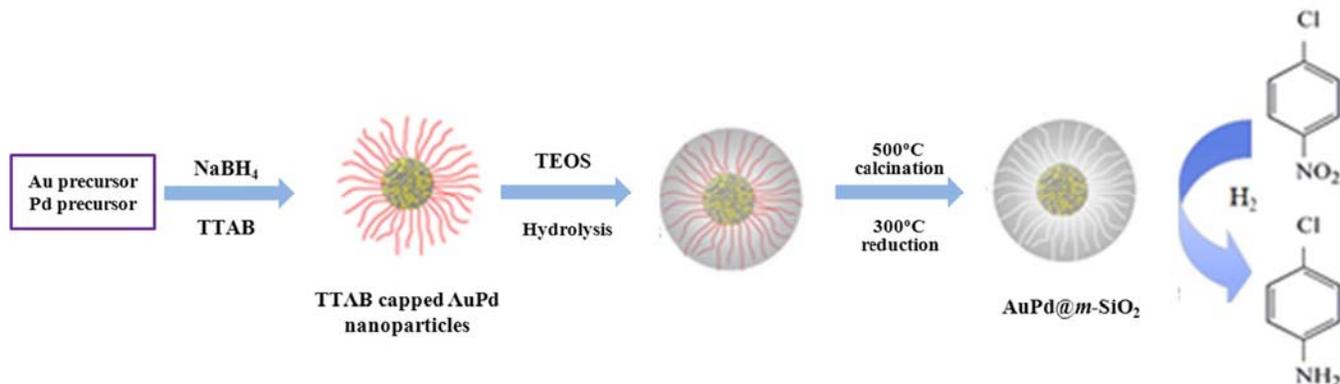


COLL 765

Building up AuPd@m-SiO₂ nanocatalyst with alloyed noble metal core and mesoporous silica shell structure: Designed composite for enhanced p-chloronitrobenzene hydrogenation selectivity

Hongfeng Yin¹, yinhf@nimte.ac.cn, Shenghu Zhou², Guangming Yang¹. (1) 1. Ningbo Institute of Material Technology and Engineering, Chinese Academy Science, Ningbo, China (2) 2. Multiphase Materials Chemical Engineering, East China University of Science and Technology, Shanghai, China

A series of AuPd@SiO₂ core-shell mesoporous nanoparticles with different Au/Pd ratio were successfully synthesized by a two-step method. The surfactant capped AuPd alloy nanoparticles were coated with mesoporous SiO₂ through hydrolysis of tetraethylorthosilicate (TEOS). The as-synthesized AuPd@SiO₂ core-shell nanoparticles with about 4 nm AuPd heteroaggregate nanoparticle cores and about 17 nm silica shells were calcined at 500 °C to remove TTAB surfactants and subsequent H₂ reduction at 300 °C to obtain AuPd@SiO₂ core-shell mesoporous nanoparticles. The results of relevant characterizations such as XRD, TEM and BET revealed that the AuPd@SiO₂ nanocatalysts were highly stable during thermal treatment and H₂ reduction when under the protection of SiO₂ shells. A series of studies of the hydrogenation of p-chloronitrobenzene (p-CNB) with H₂ were tested for Au@SiO₂, AuPd₅@SiO₂, AuPd₁₀@SiO₂, Au₁₀Pd@SiO₂, Au₅Pd@SiO₂, AuPd@SiO₂, Pd@SiO₂ nanocatalysts respectively, and the results showed that the Au-Pd interaction had dramatic influence on both conversion and selectivity performance of AuPd@SiO₂ nanocatalysts.

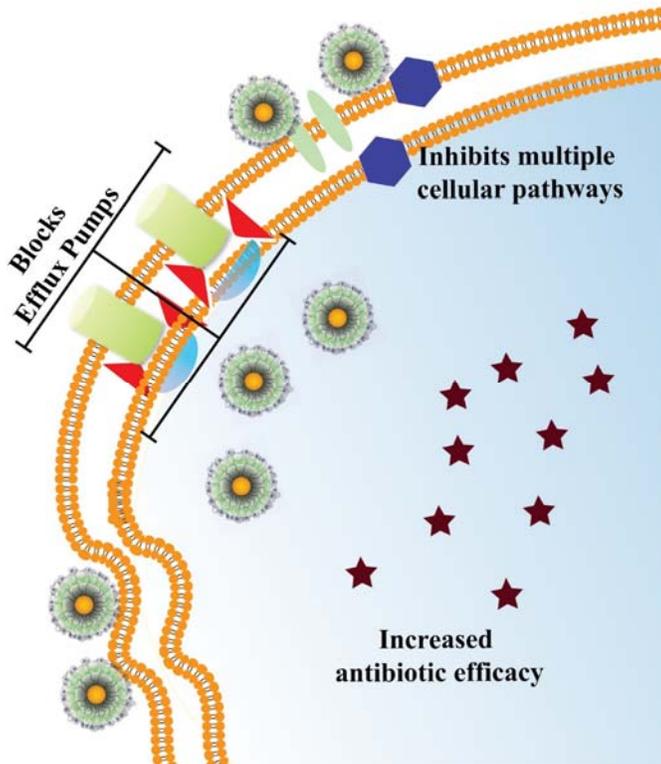


COLL 766

Synergistic antimicrobial therapy using nanoparticles and antibiotics for the treatment of multidrug-resistant bacterial infection

Akash Gupta¹, akash.umass@gmail.com, Neveen M. Saleh^{1,2}, Riddha Das¹, Ryan F. Landis¹, Arafah Bigdeli¹, Morteza Mahmoudi³, Vincent M. Rotello¹. (1) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Department of Microbiology, National Organization for Drug Control and Research (NODCAR), Giza, Egypt (3) Material Science and Engineering, EPFL, Swiss Federal Institute of Technology, Lusanne, Switzerland

The emergence of drug-resistant pathogenic bacteria constitutes one of the dominant challenges in human health. Nanomaterials have recently emerged as promising candidates to combat multi-drug resistant bacteria owing to their broad-spectrum activity. However, lack of specificity versus mammalian hosts limits the clinical practicality of current nanomaterials. Here, we report hydrophobically functionalized NPs that provide synergistic antimicrobial activity with antibiotics for combatting MDR bacterial strains. An 8–16-fold decrease in antibiotic dosage was achieved in combination therapies with engineered NPs against MDR strains. The synergy observed was attributed to the ability of hydrophobic NPs to block MDR efflux pumps of bacterial cell. Taken together, the ability of engineered NPs to target crucial pathways and localized microenvironment of bacterial infections offers new avenues to design novel antimicrobial strategies.



Schematic diagram showing the synergy between nanoparticles and antibiotics for combating resistant-bacteria.

COLL 767

Interactions between gold nanoparticles and lipid membranes: The effect of the liquid flow

Céline Molinaro, celine.molinaro@unamur.be, **Francesca Cecchet**. Laboratory of Lasers and Spectroscopies, Namur Institute of Structured Matter (NISM), NAMur Research Institute for Life Sciences (NARILIS), University of Namur (UNamur), Namur, Belgium

The study of the first contacts of nanoparticles (NPs) with cell membranes is a prerequisite either for a deep understanding of cytotoxicity mechanisms and for improving drug delivery system. Indeed, unravelling fundamental interactions of NPs with the cell barrier may help explaining macroscopic responses.

Most often, the NPs/membrane interface is studied in static conditions. However, in living systems water is motion, so that physicochemical properties and biological processes can depend on the flow parameters. Here, in order to mimic the dynamic conditions of the physiological environment, we investigated the NPs/membrane interface upon a water flow. To achieve this goal, we modelled the NPs/membrane interface through a solid-supported lipid bilayer of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) on SiO₂ in interaction with positively charged 5 nm gold NPs. Thanks to the high sensitivity of vibrational sum-frequency generation (SFG)

spectroscopy to liquid interfaces, and under dynamic conditions, we investigated the effects of the liquid flow on the above nano-bio-interface (Figure 1). We measured the vibrational response of the lipid molecules and of its close water environment, between 2800 cm^{-1} and 3600 cm^{-1} , and upon increasing flow rates, between $130\text{ }\mu\text{L}/\text{min}$ and $20\text{ ml}/\text{min}$.

With this study, we showed that the liquid motion modified the kinetics of interaction of NPs with the model membrane, and we derived a dependence on the flow rate.

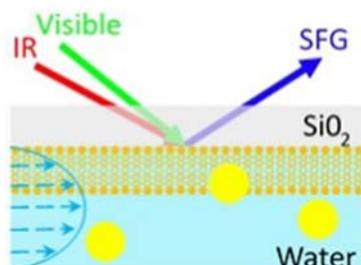


Figure 1: Schematic representation of the experimental set-up to probe the nano-bio-interface.

COLL 768

Bionano interactions of ultrasmall nanoparticles: What the cell sees in this size regime

Luca Boselli¹, luca.boselli@cbni.ucd.ie, Ester Polo^{1,2}, Valentina Castagnola³, Francesco Muraca³, kenneth dawson³. (1) University College of Dublin, Dublin, Dublin, Ireland (2) CIQUS, University Santiago de Compostela, Santiago de Compostela, Coruña, Spain (3) University College Dublin, Dublin, Ireland

When nanoparticles (NPs) are exposed to the biological milieu, they immediately get cloaked by adsorption of biomolecules (as proteins) forming the biomolecular *corona*. The formed protein cloak represents the new surface chemistry of the NPs and can alter their final fate of in the human body, for example leading to unexpected organs biodistribution. Despite the very promising role of NPs in biomedical applications, a considerable concern is still caused by the possible long-term toxicity of nanomaterials, due for example to the demonstrated tendency of NPs to accumulate in specific organs, such as liver or spleen, in an uncontrolled fashion, observed particularly in the size range of 6-100 nm. It has been shown, however, that for sizes below 3 nm certain NPs tends to exhibit efficient renal clearance and a very low concentration of these NPs was found in the liver or other filter organs. This might not be due merely to their small core size but to a different kind of interaction occurring between ultrasmall NPs (USNPs) and biomolecules. Considering that most of the plasma/serum proteins present a hydrodynamic diameter even larger than the size of USNPs, can we still speak about protein *corona* for these nanobjects?

Investigation of USNPs-proteins complex is very challenging since the protocols normally applied for larger NPs are ineffective. We obtained interesting insights on the bio-interactions of 5, 3 and 2 nm gold NPs (with a range of surface functionalisation) by using gel-electrophoresis techniques. The gel-shift assay, normally used to separate

even small peptides, allowed to observe striking differences in the way NPs with 1 nm of size difference can interact with the biological environment. Below a certain size (also strongly depending on the surface chemistry of the particle) the long-lived NP-protein interactions could be nearly eliminated, suggesting that the corona might fluctuate rapidly, possibly leading to quite distinct biological outcomes compared to larger particles.

COLL 769

Modifying the interactions between semiconductor quantum dots and bacterial targets

Denise N. Williams¹, dwill3@umbc.edu, Zheng Zheng¹, Sunipa Pramanik², Christy L. Haynes², Zeev Rosenzweig¹. (1) Chemistry and Biochemistry, University of Maryland, Baltimore County, Bowie, Maryland, United States (2) University of Minnesota, Minneapolis, Minnesota, United States

This project seeks to design a series of semiconductor luminescent quantum dots (QDs) with controlled and tunable molecular interactions with specific bacterial targets. Previous studies in our laboratory made use of optical spectroscopy, inductive coupled plasma mass spectrometry, and fluorescence microscopy to investigate the interactions between semiconductor QDs and bacteria. Results from these experiments have increased our understanding of the mechanisms of toxic interactions between semiconductor QDs and bacteria, and how to control these interactions. Additionally, we synthesized poly(oxynorborene)-coated gold nanoparticles (PON-AuNPs), and demonstrated that changes in the molecular structure of free PONs greatly impact the membrane disruption activity of free PONs and PONs-AuNPs. The current study aims to validate the hypothesis that combining the anti-bacterial activity of luminescent quantum dots with the anti-bacterial activity of PONs, by forming PONs-QDs, will lead to synergistic anti-bacterial activity.

COLL 770

Elucidating biomolecular corona role for nanoparticle interactions

Ester Polo, ester.polo@usc.es. CIQUS, University Santiago de Compostela, Santiago de Compostela, Coruña, Spain

The interaction of nanoparticles with the biological environment results in the formation of a biomolecular corona, which substantially modifies the nanoparticle pristine surface properties. Both synthetic nanoparticles in biological environment as well as naturally occurring assemblies contain all of the relevant information to understand their biological origins and likely function. Biomolecular motifs appropriately presented at the surface are implicated in specific cellular responses (for example uptake by a specific receptor pathway), cell signalling or other biological process such as activation of the immune system. Indeed, certain sequences of these bio- molecules would define how a

nanoparticle first interacts with and is recognised by cells. Moreover the organization and arrangement of these molecules on the surface it depends on nanoparticle features such as shape, size and surface chemistry.

The composition and architecture of biomolecules on the surface in turn affect the bio-interactions and thus in vivo destination. It is therefore of incredible importance and interest to deeply understand and control this bionano-interface, that ultimately mediates the interactions of nanoparticles with cells and organisms, from both a developmental and regulatory point of view. Characterizing in molecular detail the information encoded at the surface of these nano-structures is crucial to understand their biological response. It is intriguing that different nanomaterials with certain physico-chemical properties can accrete entirely different coatings and lead to specific biological outcomes.

COLL 771

β -amyloid detection in an animal model of Alzheimer's disease using glyconanoparticle

SeyedMehdi HossainiNasr, hossain5@chemistry.msu.edu. Chemistry, Michigan State University, Okemos, Michigan, United States

The number of patients who live with dementia is increasing and Alzheimer's disease (AD) is the most common type of dementia. β -amyloid ($A\beta$) accumulation and deposition in brain tissue are one of the most important hallmarks of disease. Therefore, $A\beta$ is an attractive target for imaging Alzheimer's disease. However, designing a nanoprobe with the ability to pass through the blood brain barrier (BBB) and reaching $A\beta$ plaques is a significant challenge. In this work, development and synthesis of a glyconanoparticle for in vivo imaging of $A\beta$ plaques will be presented. Briefly, characterization of this nanoprobe, its binding with $A\beta$ fibrils and in vitro ability to pass through BBB will be discussed. Then, application of this glyconanoparticle for imaging $A\beta$ plaques in an animal model of AD and related histological studies will be presented.

COLL 772

Small-angle scattering of interpenetrating polymer networks (IPNs) as medical devices with reduced risk of infection

Gregory Smith¹, gregoryneil@gmail.com, Erik Brok¹, Martin Schmiele¹, Lise Arleth¹, Kell Mortensen¹, Martin Alm², Peter Thomsen². (1) Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark (2) BioModics, Copenhagen, Denmark

A common material for urinary catheters is a hydrophobic polymer, silicone elastomer. The properties of silicone make it well-suited for producing medical devices; it has favourable mechanical properties and is chemically inert. However, this hydrophobic surface makes it prone to the adhesion of bacteria and subsequent and rapid formation

of biofilms. The bacteria that grow in biofilms tend to be resistant to antibiotic treatment, which is a serious problem. Device-associated infections present a real challenge in modern medicine, and therefore, generating materials that resist bacterial attachment and biofilm growth is a worthwhile development for reducing the number of infections.

To reduce the adhesion of bacteria and the risk of infection, at BioModics, we have produced silicone catheters and medical devices that are functionalised by the inclusion of a hydrophilic hydrogel interpenetrating polymer network (IPN). The hydrophilic polymer network is introduced by treating the hydrophobic silicone with supercritical carbon dioxide (at elevated but easily accessible temperature and pressure). This expands the silicone network, and then hydrophilic monomers are introduced to react and form an IPN within the silicone network. This hydrogel not only reduces the risk of infection, but it also has the potential to act as a drug delivery mechanism. The IPN act as a reservoir for hydrophilic small molecules that can be suspended and then controllably released at site from the IPN-impregnated silicone.

The release properties are dependent on the morphology of the IPN. However, it is a challenge to get insights to the micro structure of the IPNs. Therefore, at the University of Copenhagen, we have performed small-angle scattering measurements (with both X-rays and neutrons) to investigate the distribution of the polymer molecules within the IPN. X-ray measurements are sensitive to differences in electron density, and they primarily revealed the structure of the inorganic filler in the silicone. Neutron measurements are sensitive to isotopes, and by introducing water or heavy water (D_2O) to IPN, we were able to observe the distribution of water and the hydrophilic domains. We will discuss how studies on these nanostructured materials perform as promising future medical devices and how the structure-property relationships arising from scattering measurements are assisting optimisation of the materials for the future.

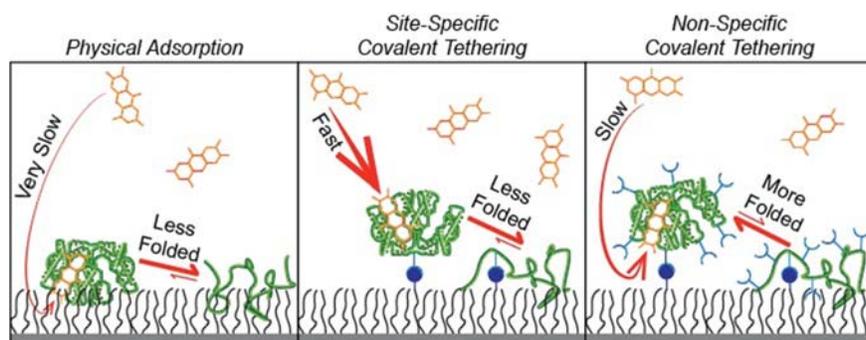
COLL 773

Correlating structural and functional heterogeneity of immobilized enzymes

Daniel F. Kienle, dfkienle@ucdavis.edu, Rebecca Falatach, Joel Kaar, Daniel K. Schwartz. Chemical Biological Eng, University of Colorado, Boulder, Colorado, United States

Many nanobiotechnology applications rely on stable and efficient integration of functional biomacromolecules with synthetic nanomaterials. Unfortunately, the reasons for the ubiquitous loss of function of immobilized enzymes remain poorly understood due to the difficulty in distinguishing between distinct molecular-level mechanisms. Here, we employ complementary single molecule (SM) methods that independently measure the structure and function (i.e., substrate binding kinetics) of nitroreductase (NfsB) that was immobilized using different bioconjugation strategies. The folding state was monitored using SM Förster resonance energy transfer, while fluorescence co-localization microscopy was used to measure SM substrate binding rates, providing a detailed picture of heterogeneous conformational dynamics and activity. Stochastic

statistical modeling methods were used to unambiguously quantify the effects of enzyme structural dynamics on enzyme function, allowing us to explicitly separate effects due to conformation and accessibility. Interestingly, we found that non-specifically tethered enzymes exhibited enhanced structural stability compared to site-specifically tethered enzymes; however, the folded state of site-specifically tethered enzymes was more active. This demonstrated an unexpected intrinsic trade-off associated with competing bioconjugation methods, suggesting that it may be necessary to balance conformational stability versus active-site accessibility. This nuanced view of enzyme immobilization will facilitate a rational approach to the integration of enzymes with synthetic nanomaterials.



COLL 774

Self-assembly of nanoparticle-protein superstructures for the direct cytosolic protein delivery to lymphoma B cells

Yuanchang Liu¹, yuanchangliu@chem.umass.edu, Xianzhi Zhang², Moumita Ray⁴, David Luther³, Vincent M. Rotello⁵. (1) Chemistry, Umass Amherst, Amherst, Massachusetts, United States (2) University of Massachusetts-Amherst, Hadley, Massachusetts, United States (3) Umass Amherst, Amherst, Massachusetts, United States (4) Chemistry, University of Massachusetts, Amherst, Amherst, Massachusetts, United States (5) Univ of Massachusetts, Amherst, Massachusetts, United States

Intracellular protein delivery is a promising avenue for biological imaging, genome engineering, and therapeutic development. The major challenge of effective delivery is to keep functional proteins in an active conformation at their site of action. Endosomal entrapment and protease-mediated degradation make standard protein delivery strategies inefficient. We have recently fabricated self-assembled superstructures through co-engineering of proteins and nanoparticles for direct cytosolic delivery to cells. These superstructures were formed by electrostatic interaction between glutamic acid-tagged recombinant proteins (E-tagged proteins) and positively-charged arginine gold nanoparticles (ArgNP). These assemblies fuse with the cell membrane, releasing the E-tagged proteins directly into the cytosol. Significantly, the E-tagged proteins retained activity after delivery, as demonstrated by gene editing of Cas9 proteins. We

will discuss the use of this delivery platform for protein and CRISPR based therapeutics for B cell lymphoma.

COLL 775

Layer-by-layer nanoparticles for the detection and treatment of ovarian cancer

Natalie Boehnke¹, nboehnke@mit.edu, **Santiago Correa**^{2,1}, **Liang Hao**¹, **Wade Wang**³, **Sangeeta Bhatia**¹, **Paula T. Hammond**^{3,1}. (1) Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (2) Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States (3) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Ovarian cancer is the fifth leading cause of cancer deaths in women. Due to poor detection methods, the majority of patients are diagnosed at stages III or IV, which have a survival rate of less than 30%. Additionally, ovarian cancers are typically not diagnosed until after metastasis has occurred, presenting additional treatment and detection challenges. Therefore, there is a need to develop new platforms to couple early detection with effective treatment methods. Layer-by-layer (LbL) electrostatic assembly can be used to generate a structured coating that can “disguise” nanoparticles (NPs) by providing a stealth outer layer while encapsulating therapeutic nucleic acids, such as small interfering ribonucleic acid (siRNA), in the inner layers. Moreover, the properties of these LbL NPs can be tuned through the choice of outer layer or incorporation of other ligands for selective delivery and uptake. Our current theranostic LbL NP design combines the use of tumor targeting outer layers and peptides with tumor specific biomarkers. Specifically, we examine siRNA-containing LbL NPs with a poly-L-aspartic acid (PLD) outer coating, which we have previously shown to have high binding to ovarian cancer cells over healthy cells. The PLD was modified with pendent propargyl groups to incorporate peptide ligands, including iRGD for additional tumor targeting and a matrix metalloproteinase responsive biomarker for tumor detection, via click chemistry. When siLuc2-containing LbL NPs were administered in subcutaneous xenograft mouse models of ovarian cancer, efficient luciferase knockdown coupled with tumor-dependent signal readout were observed, demonstrating the utility of these theranostic particles.

COLL 776

Screening for canine transitional cell carcinoma (TCC) by SERS-based quantitative urine cytology

Alessia Pallaoro^{2,1}, apallaoro@chem.ucsb.edu, **Rustin Y. Mirsafavi**³, **William T. Culp**⁴, **Gary B. Braun**⁵, **Carl D. Meinhart**⁶, **Martin Moskovits**⁷. (1) Chemistry, Simon Fraser University, Vancouver, British Columbia, Canada (2) (Primary) Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California, United States (3) Biomolecular Science and Engineering, University of California, Santa

Barbara, Santa Barbara, California, United States (4) Surgical and Radiological Sciences, University of California, Davis Veterinary Medical Teaching Hospital, Davis, California, United States (5) Sanford-Burnham Medical Research Institute, San Diego, California, United States (6) Mechanical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States (7) Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California, United States

Canine lower urinary tract neoplasia is a clinically important disease process with high mortality due to it typically having a late stage diagnosis and a poorly durable response to treatment. Non-invasive diagnostic techniques (e.g. dipstick test, urine cytology) have poor diagnostic value, while more invasive tests (e.g. cystoscopy and biopsy) are costly, often require general anaesthesia, and carry the potential to spread the disease to other sites. Here we have developed a quantitative cytological analysis method (SERS cytology) for the identification of cancerous transitional cells in urine, based on the use of multiplexed surface-enhanced Raman spectroscopy (SERS) and chemometrics analysis. The assay uses silver nanoparticle-based SERS biotags (SBTs) carrying the peptide PLZ4 (amino acid sequence cQDGRMGFc) that targets malignant transitional cells. Cells are imaged by bright field microscopy, binned according to their morphological characteristics, and those showing the hallmarks of transitional cells are analyzed by SERS-cytology, obtaining single-cell data. Transitional neoplastic cells are reliably identified by looking at the ratio of two tags -- the SERS signal produced by a bladder cancer marker (PLZ4) versus that of an internal control (a SERS marker that binds to both healthy and TCC cells equally well). Samples derived from patients diagnosed with TCC showed significantly higher mean PLZ4/TAT ratios (> 1.2) than their healthy counterparts ($p < 0.05$). The assay specificity was determined to be 83%, and sensitivity 100%, improving over the sensitivity of standard cytology. The cellular fraction of urine sediment is a highly complex medium, characterized by the presence of several types of cells. Here we show that multiplexed SERS, coupled with chemometric analysis can successfully identify transitional carcinoma cells (TCC) quantitatively in clinical urine samples.

COLL 777

Physiological stability and renal clearance of ultras-small zwitterionic gold nanoparticles: Ligand length matters

Xuhui Ning, xxn101020@utdallas.edu. Chemistry & Biochemistry, University of Texas at Dallas, Richardson, Texas, United States

Efficient renal clearance has been observed from ultras-small zwitterionic glutathione-coated gold nanoparticles (GS-AuNPs), which have broad preclinical applications in cancer diagnosis and kidney functional imaging. However, origin of such efficient renal clearance is still not clear. Herein, we conducted head-to-head comparison on physiological stability and renal clearance of two zwitterionic luminescent AuNPs coated with cysteine and glycine-cysteine (Cys-AuNPs and Gly-Cys-AuNPs), respectively. While both of them exhibited similar surface charges and the same core sizes,

additional glycine slightly increased the hydrodynamic diameter of the AuNPs by 0.4 nm but significantly enhanced physiological stability of the AuNPs as well as altered their clearance pathways. These studies indicate that the ligand length, in addition to surface charges and size, also plays a key role in the physiological stability and renal clearance of ultrasmall zwitterionic inorganic NPs.

COLL 778

Reinforcement of polymeric nanoassemblies for ultra-high drug loadings, modulation of stiffness and release kinetics, and sustained therapeutic efficacy

*Iriny Ekladiou¹, Rong Liu², Nitinun Varongchayakul¹, Luis A. Mejia Cruz³, Daniel Todd³, Heng Zhang¹, Nicholas H. Oberlies³, Robert F. Padera², Yolonda L. Colson², **Mark W. Grinstaff¹**, mgrin@bu.edu. (1) Boston University, Boston, Massachusetts, United States (2) Brigham and Women's Hospital, Boston, Massachusetts, United States (3) University of North Carolina at Greensboro, Greensboro, North Carolina, United States*

The optimization of current polymeric nanoparticle therapies is restricted by low drug loadings and limited tunability of core properties. To overcome these shortcomings, a novel self-association approach is utilized to fabricate a dual-loaded poly(1,2-glycerol carbonate)-*graft*-succinic acid-paclitaxel (PGC-PTX) conjugate nanoparticle (NP) in which the physical entrapment of free paclitaxel (PTX) affords unprecedented ultra-high drug loadings > 100 wt%, modulation of mechanical stiffness, and tunable release kinetics. Despite high incorporation of free PTX (up to 50 wt%), the dual-loaded PGC-PTX nanocarriers (i.e., PGC-PTX + PTX NPs) exhibit controlled and sustained drug release over 15 days, without burst release effects. Importantly, optimization of drug/material efficiency concomitantly affords improved *in vitro* efficacy. *In vivo*, PGC-PTX + PTX NPs are safely administered at doses exceeding the median lethal dose of standard PTX, while a single high dose significantly extends survival relative to weekly PTX administrations in a murine model of peritoneal carcinomatosis.

COLL 779

Co-aggregation of multiple drugs for chemotherapeutic delivery

***Eric Donders^{1,2}**, eric.donders@mail.utoronto.ca, Ahil N. Ganesh^{1,2}, Brian Shoichet³, Molly S. Shoichet^{4,2}. (1) Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada (2) Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada (3) Univ of Calif San Fran, San Francisco, California, United States (4) Chemical Engineering Applied Chemistry, University of Toronto, Toronto, Ontario, Canada*

Many small molecule drug-like compounds are hydrophobic and form colloidal aggregates above a critical aggregation concentration. Colloidal aggregation has been identified as the major cause of false hits in high-throughput drug screening and can also cause false negative results in cell-based assays. However, if these drugs could be

reformulated to take advantage of their tendency to aggregate, new therapies could be discovered that would have been otherwise overlooked.

Drug-loaded nanoparticles have been increasingly investigated for their ability to treat disease while minimizing side effects. As nano-sized particles consisting almost entirely of drug, colloidal drug aggregates are well-suited to this role. Recently, a series of strategies has been explored to exploit the tendency of these molecules to aggregate with the goal of using the particles as drug delivery vehicles. We are now interested in improving treatment efficacy by designing formulations that contain multiple therapeutic compounds.

Here, we investigate the properties of colloidal drug aggregates comprising multiple anticancer drugs. We demonstrate that these self-assembled structures can be stabilized in physiological conditions by small amounts of amphiphilic polymers, and that co-aggregation increases the colloidal stability of crystallization-prone drugs.

Specifically, we aimed to stabilize a small molecule breast cancer drug which transiently forms colloids, but precipitates completely within 24 hours. We found that co-aggregation with a second breast cancer drug produced colloidal drug aggregates that were stable for multiple days.

By better understanding the physical chemistry and biological fate of drug colloids, new formulation strategies for difficult to deliver drugs can be developed.

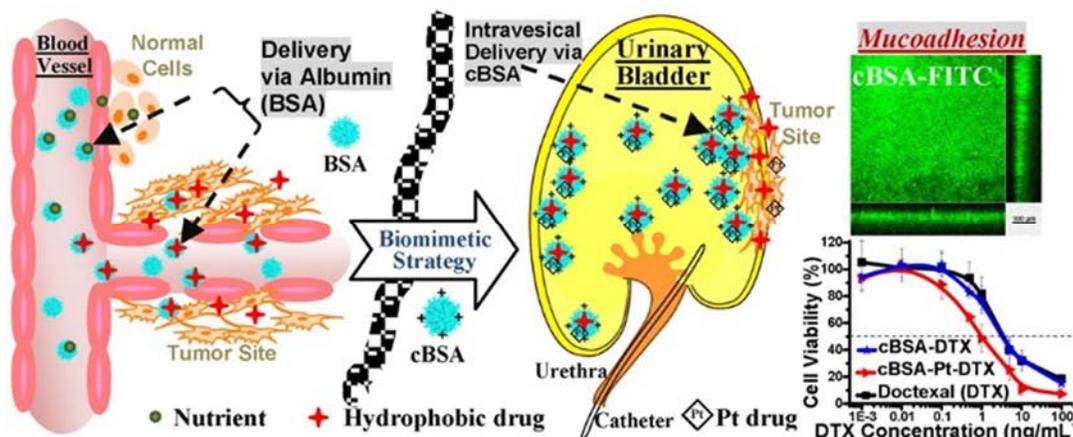
COLL 780

Cationized albumin carrier for potential synergistic chemotherapy of non-muscle-invasive bladder cancer

*Shengjie Lu, Juwita Rahmat, Ratha Mahendran, En Tang Kang, Edmund Chiong, **Koongee Neoh**, chenkg@nus.edu.sg. National University of Singapore, Singapore, Singapore*

Serum albumin is a well-known protein, acting as an intravascular transporter of hydrophobic nutrients and drugs in the blood circulatory system. We investigated the potential of using a cationic formulation of albumin (cBSA) as a delivery vehicle for intravesical delivery of cisplatin (CDDP) and docetaxel (DTX) against non-muscle-invasive bladder cancers. CDDP was loaded into the cBSA via coordination binding whereas DTX was loaded via hydrophobic interactions. The cBSA carrier prevented burst release of the loaded drugs and also enabled the loaded drugs to be readily taken in by UMUC3 bladder cancer cells. As a result, the dual drug-loaded cBSA complex exhibited enhanced killing efficacy against UMUC3 cells after 4 h-treatment *in vitro* as compared to the respective single drug-cBSA complex or non-cationized BSA loaded with the two drugs. Obvious synergy arising from the simultaneous delivery of the two drugs into the cells was indicated from the combination index. *Ex vivo* experiments with porcine bladder showed that cBSA, unlike BSA, attached readily onto the bladder luminal surface without causing extensive damage to the urothelium. Similarly, *in vivo* tests with mice, instilled FITC-labeled cationic albumin showed longer retention and greater penetration into the glycosaminoglycan layer on the urothelium surface than the corresponding non-cationized albumin. Thus, our study demonstrates that cationized

albumin, with its mucoadhesive property and capacity for loading multiple synergistic drugs and releasing them in a sustained manner, is potentially a promising drug carrier for intravesical chemotherapy against bladder cancer.



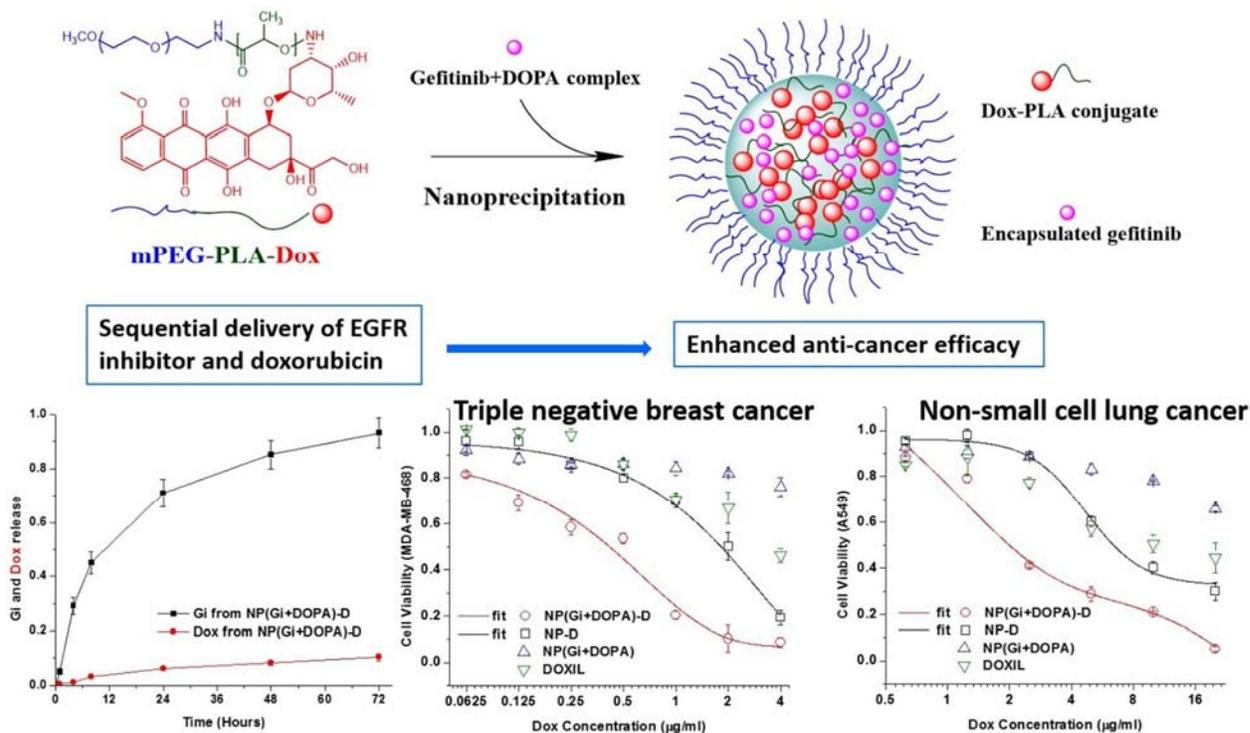
Schematic diagram illustrating biomimetic intravesical delivery via protein to bladder

COLL 781

Sequential co-delivery of EGFR inhibitor and doxorubicin for targeted combination chemotherapy

Joo-Youp Lee¹, joo.lee@uc.edu, **Zilan Zhou**¹, **Mina Jafari**¹, **Vishnu Sriram**². (1) ChE, DBCEE ML0012, University of Cincinnati, Cincinnati, Ohio, United States (2) Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio, United States

There are an increasing number of studies showing the order of drug presentation plays a critical role in achieving optimal combination therapy. Here, a nanoparticle design is presented using ion pairing and drug-polymer conjugate for the sequential delivery of epidermal growth factor receptor (EGFR) inhibitor and doxorubicin (Dox) targeting EGFR signaling applicable for the treatment of triple negative breast cancer and non-small cell lung cancer. To realize this nanoparticle design, EGFR inhibitor complexed with dioleoyl phosphatidic acid (DOPA) via ion pairing was loaded onto the nanoparticle made of Dox-conjugated poly(L-lactide)-block-polyethylene glycol (PLA-*b*-PEG) and with an encapsulation efficiency of ~90%. The nanoparticle system exhibited a desired sequential release of EGFR inhibitor followed by Dox, as verified through release and cellular uptake studies. The nanoparticle system demonstrated approximate fourfold and threefold increases in anti-cancer efficacy compared to a control group of Dox-PLA-PEG conjugate against MDA-MB-468 and A549 cell lines in terms of half maximal inhibitory concentration (IC₅₀), respectively. High tumor accumulation of the nanoparticle system was also substantiated for potential *in vivo* applicability by non-invasive fluorescent imaging.



COLL 782

Highly engineered platinum nanoparticles as multifunctional active nanocarriers integrating the function of high-performance antioxidant drugs

Mauro Moglianetti, mauro.moglianetti@iit.it. CBN, Italian Institute of Technology, Lecce, Italy

Our recent findings show that pure, biocompatible platinum nanoparticles (Pt NPs) are able to counteract molecular dysfunctions that cause accumulation of intracellular reactive oxygen species (ROS).

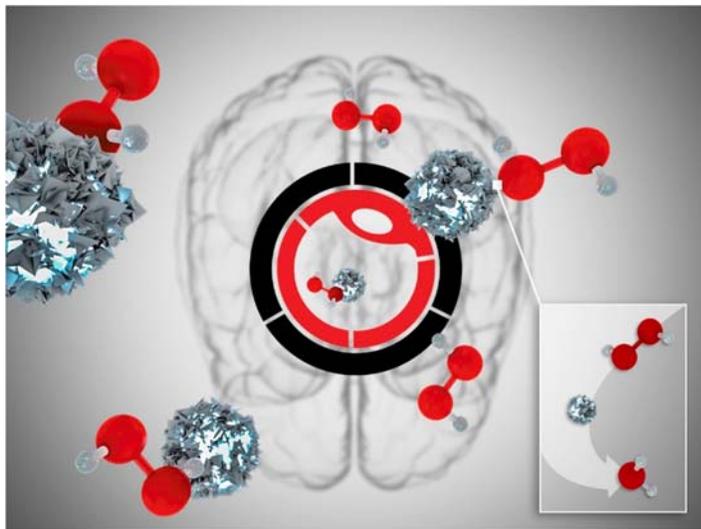
After performing a systematic characterization of Pt NPs as biocompatible and antioxidant materials, we demonstrated, for the first time, that Pt nanozymes are capable to restore physiological ROS homeostasis in a *real experimental model* of a human cerebrovascular disease, namely Cerebral Cavernous Malformation (CCM). CCM is characterized by an increased level of intracellular ROS, and we found that Pt nanozymes can *completely* recover the cellular phenotype, similar to that of wild type cells.

This is possible because of the strong and broad anti-oxidant nanozyme activity of Pt NPs, which are simultaneously endowed with strong catalase-, peroxidase-, and superoxide dismutase-like activities, with superior performance than natural enzymes and higher adaptability/resistance to changes in environmental conditions.

These findings are important and of broad interest, and open up novel perspectives in nanomedicine for the development of multifunctional active nanocarriers integrating the function of high-performance antioxidant drugs, with strong potential for therapies of

complex oxidative stress-related diseases.

We will also present our latest data on the importance of platinum nanoparticles shape (octahedral vs spherical) in the development of nano-carrier with selective enzymatic activity, uptake and drug-delivery properties.



COLL 783

Fast releasing oral formulation of clofazimine nanoparticles prepared via flash nanoprecipitation as anti-cryptosporidiosis therapeutics

Yingyue Zhang¹, zhangyingyue2296691@gmail.com, Jie Feng¹, Simon McManus¹, Kurt Ristorph¹, Robert K. Prudhomme². (1) Chemical and Biological Engineering, Princeton University, Franklin Park, New Jersey, United States (2) Dept. of Chemical Biological Engineering, Princeton University, Princeton, New Jersey, United States

Cryptosporidiosis is a leading cause of diarrhea in small children in the developing world, caused by *Cryptosporidium* infections reside in the intestine. It results in severe symptoms such as dehydration, vomiting, and fever, if patients are not provided with fast acting treatment. Clofazimine, a lipophilic riminophenazine antibiotic with $\log P=7.66$, was recently identified as a lead hit for *Cryptosporidiosis*. It was classified as class II drug due to its poor aqueous solubility but high permeability. In this study, we developed clofazimine nanoparticles with three biocompatible stabilizers, namely, hypromellose acetate succinate (HPMCAS), lecithin, and zein, using Flash Nanoprecipitation Technology with high encapsulation efficiency (>93%). To convert liquid suspension to redispersible nanoparticle powders for ease of drug storage and transportation, standard drying approach lyophilization as well as scalable spray drying were explored. The release behaviors of clofazimine nanoparticles prepared by different surface coatings were studied by a media-swap dissolution test in simulated gastric and intestinal fluid. The raw clofazimine powder and its commercial product Lamprene® were also included as comparison. To understand the significantly improved dissolution rates observed with nanoparticle formulations, differential scanning calorimetry and

scanning electron microscopy were used to characterize the nanoparticle powders. In addition, *In vivo* pharmacokinetics study was carried out in rats to understand the oral bioavailability difference between clofazimine nanoparticles stabilized by distinct stabilizers.

COLL 784

Solid drug nanoparticles synthesised using spontaneous nanoprecipitation of tenofovir disoproxil fumarate: From proof of concept to *in vivo* pharmacokinetics of improved oral dosage

James J. Hobson¹, j.hobson@liverpool.ac.uk, Paul Curley², Amer Al-khouja³, Marco Siccardi², Charles Flexner³, Caren L. Meyers³, Andrew Owen², Steve Rannard¹. (1) Department of Chemistry, University of Liverpool, Liverpool, United Kingdom (2) Molecular and Clinical Pharmacology, University of Liverpool, Liverpool, United Kingdom (3) Pharmacology and Molecular Sciences, Johns Hopkins School of Medicine, Towson, Maryland, United States

Improved delivery and pharmacokinetics of oral therapeutic compounds is of great importance in the development of drug formulations. This is particularly true for chronic, life-long conditions such as HIV, where there is an associated pill burden and high dosage for patients, with the need for strict compliance with antiretroviral (ARV) regimens. Advances have been made in the nanoformulation of hydrophobic drug compounds, however, water soluble ARVs (e.g. tenofovir disoproxil fumarate, TDF) are not suitable for common nanoformulation approaches, such as milling or Oil-in-Water emulsion templating.

We describe a novel nanoformulation strategy in which Solid Drug Nanoparticles (SDNs) of TDF were synthesised using a spontaneous methanol in dichloromethane nanoprecipitation method. Binary combinations of W/O stabilisers were assessed, and it was shown that nanoprecipitation occurred when the clinically-utilised dioctyl sulfosuccinate (AOT; also known as docusate sodium). Nanoprecipitations of up to 80 wt% active loading could be directly generated after addition of an oily dispersal media and freeze drying to remove volatile organic solvents, after which the formulation was ready for dosage as a homogenous oily liquid. No further processing or dispersal of the samples was required, making this a quick, facile, direct route to product formation. Nanoparticle hydrodynamic diameters of candidate nanoprecipitations ranged from 100 to 300 nm as determined by dynamic light scattering (DLS). Isothermal Titration Calorimetry (ITC) analysis demonstrated interactions between AOT and TDF, potentially displacing the fumarate group and forming a new ion pairing, resulting in the formation of the nanoprecipitate.

Subsequently, 80 wt% loaded TDF nanoprecipitates, stabilised by a 1:1 mixture of AOT and either Lauroglycol FCC or Maisine 35-1, dispersed in a range of biocompatible oils underwent pharmacokinetic analysis (PK) in rodents via oral gavage. The results showed absorption of TDF nanoprecipitations and subsequent plasma conversion to

parent tenofovir (TFV), with both an oil effect and stabiliser effect observed in relation to TFV concentrations in plasma.

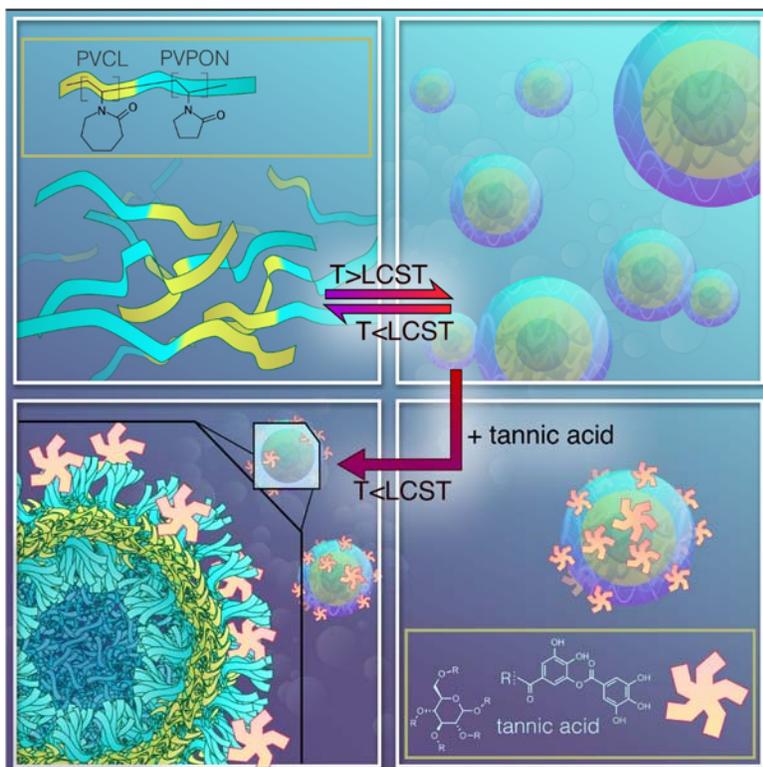
These data show that TDF can be loaded at very high concentrations and homogeneously dispersed within an orally-dosable oil, with subsequent drug delivery to the systemic circulation after oral administration, offering a promising approach to developing SDN formulations of water soluble compounds with clinical benefits.

COLL 785

Polymersomes based on temperature-sensitive poly(N-vinylcaprolactam) for anticancer therapy

Veronika A. Kozlovskaya, vkozlovs@uab.edu, Aaron Alford, Eugenia P. Kharlampieva. Chemistry Department, University of Alabama at Birmingham, Birmingham, Alabama, United States

We report a versatile synthesis for polymersomes of controlled submicron (<500 nm) size for intracellular delivery of high and low molecular weight compounds. The nanoparticles are synthesized by stabilizing the vesicular morphology of thermally responsive poly(N-vinylcaprolactam)_n-b-poly(N-vinylpyrrolidone)_m (PVCL_n-b-PVPON_m) diblock copolymers with tannic acid (TA), a hydrolyzable polyphenol, via hydrogen bonding at the temperature above the copolymer's LCST. The PVCL₁₇₉-b-PVPON_m diblock copolymers are produced by controlled RAFT polymerization of PVPON using PVCL as a macro-chain transfer agent. The size of the TA-locked (PVCL₁₇₉-b-PVPON_m) polymersomes at room temperature and upon temperature variations are controlled by the PVPON chain length and TA:PVPON molar unit ratio. We also show that TA-locked polymersomes can encapsulate and store the anticancer drug doxorubicin (DOX) and higher molecular weight dextrans in the physiologically relevant pH and temperature range. Encapsulated DOX releases in the nuclei of human alveolar adenocarcinoma tumor cells after 6-h incubation via biodegradation of the TA shell with the cytotoxicity of DOX-loaded polymersomes being concentration-dependent. Our approach offers biocompatible and intracellular degradable nanovesicles of controllable size for delivery of a variety of encapsulated materials and provides a new perspective for fundamental studies on thermo-triggered polymer assemblies in solutions.



The scheme shows that PVCL_n-b-PVPON_m diblock copolymers assembled into polymersomal nanocapsules at T > LCST can be locked with TA via hydrogen bonds with PVPON, which results in PVCL_n-PVPON_m nanocapsules stable at T < LCST.

COLL 786

Hybrid viral/nonviral gene carriers for molecularly targeted, versatile cancer therapy

Margaret Lugin¹, mlugin@uci.edu, **Kirolos Kelada**¹, **Angela Fleischman**², **Young J. Kwon**³. (1) Chemical Engineering, University of California, Irvine, Costa Mesa, California, United States (2) School of Medicine, University of California, Irvine, Irvine, California, United States (3) Chems, Uci, Irvine, California, United States

Many cancers are caused by kinase domain mutations, leading to the prevalence of tyrosine kinase inhibitors (TKIs) as an industry standard of care. These drugs target a specific mutation pathway, making them more effective than traditional chemotherapy treatments. Yet often TKI therapies are incomplete and many patients develop resistance to TKIs, which could be mitigated by molecular therapy tackling the same target at a genetic level. However, the success of gene therapy is dictated by efficient vehicles including both viral and nonviral carriers. Viral/nonviral hybrid vectors integrate the advantages of both forms such as avoided immune response, ensured efficient genome integration, if desired incorporation of a second therapeutic modality, and greatly expanded means of engineering multi-modal therapeutic platforms. This work focuses on developing hybrid nonviral/viral nanoparticles made from a

ketalized acid-degradable shell, encapsulating an adeno-associated virus (AAV) core. Within the shell, siRNA is incorporated, to deliver both DNA from the virus and siRNA, thus a multi-modal therapy. The ketalized shell should breakdown in endosomal conditions, allowing for effective release of the therapeutic AAV and RNA. To confirm virus encapsulation, size was determined by DLS and surface charge was found using zeta potential. Acid-hydrolysis of the resulting viral/nonviral hybrid vectors confirmed both encapsulation and release of AAV and siRNA. As model therapeutic targets, viral/nonviral hybrid vectors were prepared to express pro-apoptotic Bim AAV and simultaneously silence pro-survival Mcl-1 in leukemia and lung cancers with kinase mutations. The general toxicity of the platform was assessed by delivering to various non-mutated controls of the cancers. Results demonstrated that only mutated cell lines were affected by treatment and the viral/nonviral hybrid vectors were more effective than either component on its own, giving a synergistic effect between the DNA and siRNA. This talk will discuss the formation of the hybrid particles, as well as their potential as a candidate for cancer therapy.

COLL 787

Cellulose-based photonic nanomaterials for biomedical imaging

Berney Peng¹, berney.peng@tufts.edu, **Mohammad Almeqdadi**^{2,3}, **Fabrice Laroche**⁴, **Shajesh Palantavida**⁵, **Saqib Ahmed Peerzade**¹, **Maxim Dokukin**¹, **Jatin Roper**^{6,3}, **Hui Feng**⁴, **Igor Sokolov**⁷. (1) Tufts University, Medford, Massachusetts, United States (2) Medicine, St. Elizabeth Medical Center, Brighton, Massachusetts, United States (3) The David H. Koch Institute for Integrative Cancer Research at MIT, Cambridge, Massachusetts, United States (4) Pharmacology and Experimental Therapeutics, Boston University, Boston, Massachusetts, United States (5) Suite 2600, Tufts University, Medford, Massachusetts, United States (6) Gastroenterology, Tufts University School of Medicine, Boston, Massachusetts, United States (7) Dept of Mech Eng, Biom, 204 Anderson Hl, Tufts University, Medford, Massachusetts, United States

Fluorescent, targeting nanoparticles are a contemporary solution for biomedical imaging and diagnostics of cancer. Particles can be used to label intra- and extracellular biomarkers and provide key information for clinical decisions based on high resolution, real-time optical imaging while mitigating off-target immunogenic effects. Here, we utilize cellulose acetate to develop a class of natural and inert fluorescent nanomaterials possessing well-defined safety profiles. Particles are generated from supramolecular assemblies of cellulose acetate and guest polymers, producing composite materials with good biocompatibility, tunable morphology, physical encapsulation ability, and excellent luminescence. We demonstrate effective *in vivo* targeting of sub-mm tumors in zebrafish cervical cancer xenografts as well as topical targeting of colon cancer tumors in mice.

COLL 788

Biodegradable periodic shRNA systems for enhanced gene silencing

Connie Wu¹, conniewu@mit.edu, **Jiahe Li**¹, **Wade Wang**¹, **Paula T. Hammond**². (1) *Massachusetts Institute of Technology, Cambridge, Massachusetts, United States* (2) *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States*

RNA interference (RNAi) provides a versatile therapeutic strategy via silencing of specific genes implicated in cancer and other diseases. However, clinical translation of RNAi for cancer therapeutics remains unrealized, due to challenges in delivery of small interfering RNA (siRNA) to tumors. The low valency and high rigidity of siRNA often requires high excesses of cationic delivery materials to condense into stable nanoparticles, leading to dose-limiting toxicities. To address this challenge, we adopt an RNAi platform based on periodic short hairpin RNAs (p-shRNAs). Consisting of siRNA sequences linked together, these polymeric RNAi molecules are generated by the repeated action of an RNA polymerase around a small circular DNA template. Through template design and selective enzymatic digestion, we can design p-shRNA structures that are efficiently processed inside cells into siRNAs and induce significant gene silencing. Furthermore, p-shRNA exhibits immunostimulatory properties that can be combined with RNAi to dramatically enhance therapeutic efficacy.

To develop an optimal delivery vehicle for op-shRNA, we used factorial design to synthesize a library of poly(beta-amino ester)s (PBAEs). Screening of this library showed that p-shRNA silencing efficiency increases with increasing alkyl side chain percentage and decreasing molecular weight. Our PBAEs are able to fully condense p-shRNA into sub-100 nm complexes with high silencing efficiency, at much lower polymer-to-RNA ratios than those typically required for PBAE gene delivery. We further modified the complexes with a poly(ethylene glycol) (PEG)-PBAE copolymer containing alkyl side chains, introducing an outer PEG layer that can enhance colloidal stability and decrease cytotoxicity. By directing op-shRNA against signal transducer and activator of transcription 3 (STAT3), which promotes an immunosuppressive tumor microenvironment, we can significantly reduce tumor progression and prolong survival in a B16F10 melanoma model. Thus, through nucleic acid engineering and rational carrier design, we have successfully developed a stable, potent RNAi delivery system that can trigger significant gene silencing at low doses, and enable higher therapeutic efficacy *in vivo* through RNA interference.

COLL 789

Size characterization of micelles and microemulsions by Taylor dispersion analysis

Vincent Jannin^{1,2}, vjannin@Gattefosse.com, **Hervé Cottet**³. (1) *Gattefossé R&D, St-Priest, France* (2) *Université Claude Bernard, Lyon, France* (3) *CNRS, ENSCM, Université de Montpellier, Montpellier, France*

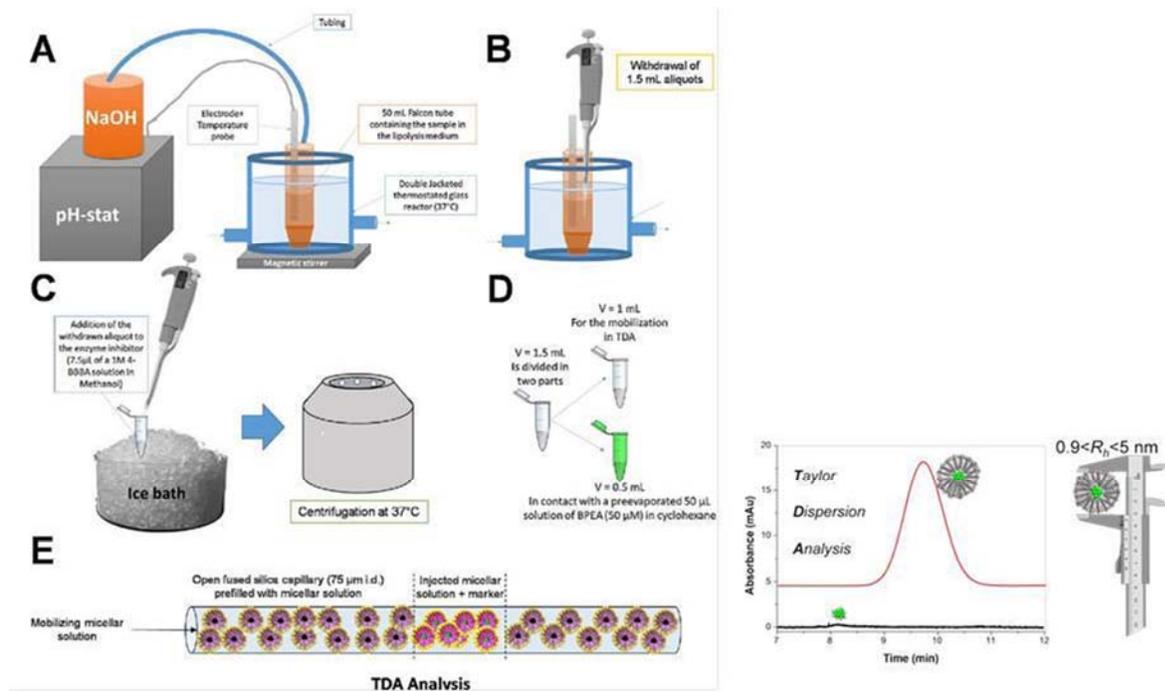
Micellar systems and microemulsions are commonly for improving solubilization and dispersion of hydrophobic / poorly soluble drugs. Of critical importance during the drug

development process is the ability to reliably and rapidly characterize these micellar/microemulsion systems: for their ability to disperse and then release the drug in the dissolution media; the consistency of the release profile; and potential changes to their properties following intake due to digestion using in-vitro models, in the presence of lipolytic enzymes.

Commonly used analytical techniques like small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), dynamic light scattering (DLS) and NMR are powerful but which may be affected by the presence of aggregates or by the high viscosity of the solution; SAXS and SANS require a model for data treatment; and SANS requires a synchrotron which is not always easily accessible. In this context, Taylor dispersion Analysis (TDA) may be an interesting alternative.

TDA is a simple and absolute method that determines the molecular diffusion coefficient and hydrodynamic radius of a wide variety of molecules (proteins, polymers, small molecules, nanoparticles...) having a size ranging between the Å and up to nearly 300 nm. It is based on the analysis of the band broadening of a solute plug in a laminar Poiseuille flow. The peak variance of the elution profile allows the quantification of the molecular diffusion coefficient.

The aim of this presentation is share recent developments in the use of TDA for differentiating micellar (cationic, anionic, neutral and zwitterionic) systems and the radii for microemulsions; the choices of micellar marker and the influence the surfactant/marker concentrations in TDA; the experimental set up vis-à-vis other analytical methods; and the interpretation of the data from self-emulsifying drug delivery systems.



COLL 790

Polymeric micelles for therapeutic delivery of hydrogen sulfide

Urara Hasegawa¹, *hasegawa@ksu.edu*, **Andre van der Vlies**², **Jerry J. Chen**³. (1) *Chemical Engineering, Kansas State University, Manhattan, Kansas, United States* (2) *Chemical Engineering, KSU, Manhattan, Kansas, United States* (3) *Osaka University, Osaka, Japan*

Hydrogen sulfide (H₂S) serves as a gaseous signal-transmitter molecule in the human body that regulates inflammation, relaxes vascular smooth muscles, promotes angiogenesis and mediate neurotransmission. With the discovery of the biological significance of H₂S, the potential for H₂S-based therapy has attracted growing attention. However, due to its volatile nature and a short half-life under physiological conditions, development of a H₂S delivery system which enables the release of H₂S at the site of interest in a controlled manner is needed in order to explore its therapeutic potential. One common approach is to use H₂S donor compounds including anethole dithiolethione (ADT) derivatives which generate H₂S under physiological conditions. However, the fast and uncontrolled rate of H₂S release, toxic side effects of the donor compounds and/or their decomposition products as well as rapid renal clearance remain as the major problems associated with the use of small H₂S donor compounds. To address this issue, we developed nano-sized gas donors based on polymeric micelles (H₂S donor micelles) which enable sustained H₂S release under physiological conditions. Here, we report design, synthesis and characterization of polymeric H₂S donor micelles containing anethole dithiolethione (ADT) moieties. Furthermore, the proangiogenic and anti-apoptotic activities of these micelles were evaluated in the in vitro cell culture assays as well as the in ovo chick chorioallantoic membrane (CAM) assay.

COLL 791

Complexation loading of antimicrobial peptides into microgel-modified surfaces

Jing Liang, *jliang4@stevens.edu*, **Matthew Libera**. *Chemical engineering and Materials Science, Stevens Institute of Technology, Hoboken, New Jersey, United States*

Various strategies have been applied to inhibit chronic infection associated with tissue-contacting biomedical devices. Traditional drug delivery based on the elution of antimicrobials from has been extensively explored. However, this method often releases its loaded antimicrobials before being challenged by bacteria. Here, we demonstrate an approach that first modifies a synthetic surface with anionic microgels and subsequently loads them by complexation with cationic antimicrobials. Significantly, these complexed antimicrobials can be sequestered for extended time periods including in particular cases multiple weeks under physiological condition appropriate for combating bacterial colonization of implanted biomedical devices.

Lightly crosslinked poly(acrylic acid) microgels were electrostatically deposited onto poly(allyamine hydrochloride)-primed glass substrates and their response to various solution conditions was followed by *in situ* optical and confocal microscopy. The osmotic swelling of microgels was observed in neutralized low ionic strength buffers. The addition of cationic antimicrobials (e.g. colistin, L5, Sub 5) led to microgel deswelling because of antimicrobial-microgel complexation. By eluting the antimicrobial-complexed microgels into buffers with varying pH and ionic strength, the stabilization of antimicrobial-microgel complexation was studied. Microgel reswelling indicated antimicrobial elution into the surrounding buffer. In general, high ionic strength and low pH usually result in a rapid release of antimicrobials. Moreover, the loading and release of cationic antimicrobials with different physiochemical properties (molecular weight, charge density, hydrophobicity) was studied. For small cationic antibiotics, complexation loading was rapid and within one minute. However, they released rapidly under physiological ionic strength and pH. For larger antimicrobial peptides with more hydrophobicity, the loading process took longer and resulted in more stable complexation able to resist elution into physiological buffer. Antimicrobials with higher charge density also showed stronger complexation and could be sequestered within the microgels for 30 days under physiological conditions. Despite being strongly complexed within the microgels, these antimicrobial-loaded microgel-modified surfaces were able to resist bacterial colonization by actively killed bacteria.

COLL 792

Novel, self-assembled PLGA-PEG-PLGA nanogels, utilizing multiple non-covalent interactions for the extended and controlled release of nucleic acid conjugates to treat secondary cataracts

Laura L. Osorno¹, osornol3@students.rowan.edu, Robert Getts³, Mindy George-Weinstein², Mark Byrne¹. (1) Biomedical Engineering, Rowan University, Glassboro, New Jersey, United States (2) Division of Research, Philadelphia College of Osteopathic Medicine, Philadelphia, Pennsylvania, United States (3) Research & Development, Genisphere, LLC, Hatfield, Pennsylvania, United States

Cataracts are the second leading cause of blindness worldwide. There are over 100 million cataract surgeries each year, and these cases are expected to double within the next ten years. 20% of adults and nearly all children develop secondary cataracts, or posterior capsule opacification (PCO), following cataract surgery. This vision impairing disorder is characterized by fibrosis, wrinkles in the lens capsule, and aggregates of differentiating lens epithelial cells. Currently, Nd:YAG laser therapy is used to treat PCO; however, laser is not available worldwide and adverse effects on surrounding ocular tissues may arise. Thus, there is a considerable unmet need for more efficacious and convenient treatments for PCO. Our work focuses on engineering novel, injectable, biodegradable, physically crosslinked nanogels that provide prolonged bioavailability, as well as extended and controlled release of 3DNA® nanocarriers that target the cells responsible for PCO.

Novel, *in-situ* gelling nanogels consisting of poly(lactic-co-glycolic acid)-b-poly(ethylene glycol) (PLGA-PEG) triblock copolymer and poly(L-Lysine) (PLL) that self-assemble at physiological temperatures and are optically clear were designed. Nanogels with lactic acid (LA) to glycolic acid (GA) ratios between 3 and 15, solution compositions between 10 and 25% (w/v), and PLGA/PEG ratio between 1 and 3, were characterized via rheology and UV-Spectroscopy. Hydrogel formulations with LA/GA ratio of 15/1, at compositions between 20 and 25% (w/v), and PLGA/PEG ratio of 2/1 allow for over 90% visible light transmittance, gel formation at 35 °C, and sustained release of 3DNA over two weeks. Microfluidic devices that mimic the physiological flow rate in the lens capsule were designed to study drug release kinetics controlled by non-covalent interactions and degradation of PLGA-PEG-PLGA via the cleavage of ester bonds. Continuous and extended release of 3DNA conjugates occurred over a period of four weeks through non-covalent interactions between PLL and 3DNA, at PLL concentrations between 10 and 80% (w/v).

The physical states of this novel, injectable, optically clear hydrogel can be easily modified for the purpose of modulating drug release kinetics. This formulation will be useful for sustained delivery of 3DNA conjugates designed to target cells that cause PCO. Our US patent pending technology offers a potentially more effective delivery method for other therapeutics to treat ocular diseases.

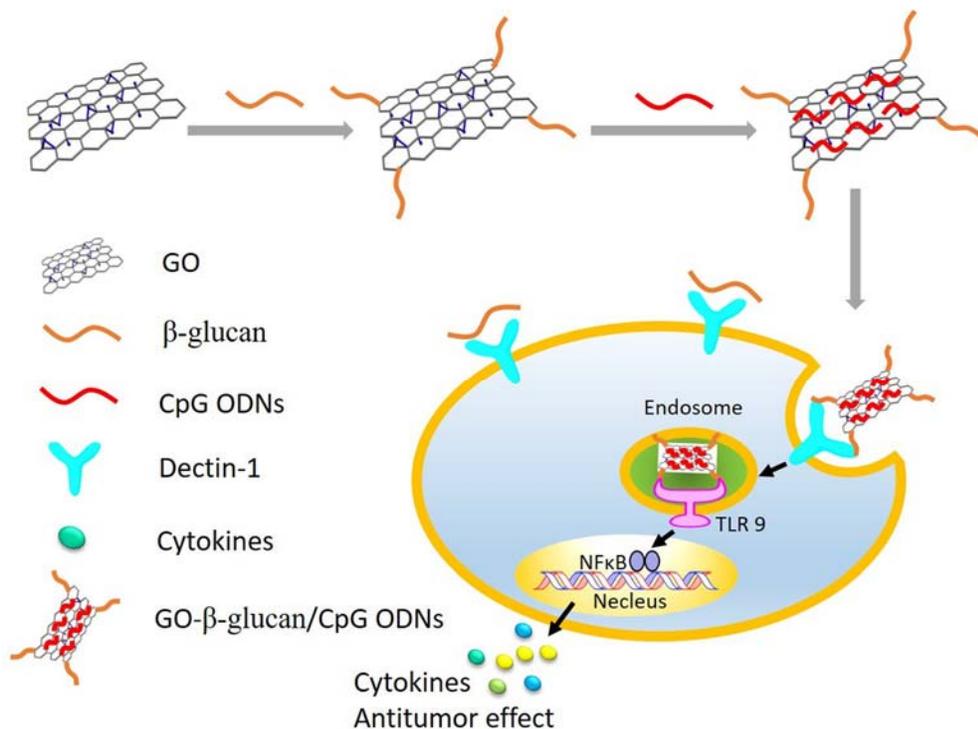
COLL 793

Yeast β -glucan functionalized graphene oxide for targeted delivery of CpG ODNs and enhanced cancer immunotherapy

Huijie Zhang, zhj0502@jiangnan.edu.cn, Jinghua Chen. School of Pharmaceutical Sciences, Jiangnan University, Wuxi, China

CpG oligodeoxynucleotides (CpG ODNs) possess immunostimulatory activity, which stimulate innate and adaptive immune responses by activation of Toll-like receptor 9 (TLR 9). Thus, CpG ODNs show strong potential as immunotherapeutic agents against various diseases. *In vitro* and *in vivo* studies have evidenced the efficacy of CpG ODN in cancer immunotherapy. However, therapeutic efficacy of CpG ODNs are largely limited due to their extreme susceptibility to nuclease degradation and poor cellular uptake. Therefore, development of efficient delivery systems capable of delivering CpG ODNs into target immune cells is crucial to enhance their therapeutic efficacy. In this study, we developed a novel targeted CpG ODNs delivery system based on yeast β -glucan functionalized graphene oxide (GO) and further investigated its efficacy in cancer immunotherapy (Scheme). Yeast β -glucan possess immunostimulatory and antitumor activity, which can be recognized by the Dectin-1 expressed by immune cells. The functionalization of GO with β -glucan decreased the non-specific protein adsorption and improved its biocompatibility. β -glucan functionalization endowed the delivery system with macrophage targeting ability due to its recognition with Dectin-1. GO- β -glucan efficiently delivered CpG ODNs into RAW264.7 cells and synergistically enhanced cytokines secretion. GO- β -glucan/CpG ODNs complexes exhibited potent

immunostimulatory activity and were effective in inhibiting tumor cells growth. These results suggested that β -glucan could not only work as targeting moiety for immune cells but also function synergistically with CpG ODNs in inducing antitumor effect. Taken together, GO- β -glucan/CpG ODNs complexes have strong potential in cancer immunotherapy.



Schematic illustration shows the preparation of targeted CpG ODNs delivery system based on GO- β -glucan and their synergistically enhanced antitumor effect

COLL 794

Time-lapse live cell imaging to monitor doxorubicin release from DNA origami nanostructures

Risheng Wang¹, wangri@mst.edu, Yun Zeng¹, Jiajun Liu², Shuo Yang¹, Wenyan Liu¹, Liang Xu². (1) Chemistry, Missouri University of Science and Technology, Rolla, Missouri, United States (2) Molecular Biosciences, The University of Kansas, Lawrence, Kansas, United States

Self-assembled DNA nanostructures have attracted significant research interest in biomedical applications because of their excellent programmability and biocompatibility. To develop multifunctional drug delivery from DNA nanostructures, considerable key information is still needed for clinical application. This includes elucidation of the mechanism of drug release from DNA origami, quantification of drug cellular distribution,

and the influence of the geometry of DNA architectures on drug delivery efficiency. Traditional fixed endpoint assays do not reflect the dynamic and heterogeneous responses of cells with regard to drugs, and may lead to the misinterpretation of experimental results.

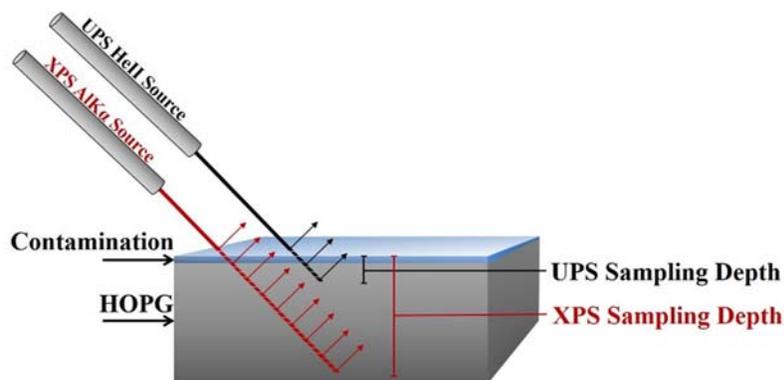
For the first time, an integrated time-lapse live cell imaging system was used to study the cellular internalization and controlled drug release profile of three different shaped DNA origami/doxorubicin (DOX) complexes for three days. Our results demonstrated the dependence of DNA nanostructures on shape for drug delivery efficiency, while the rigid 3D DNA origami triangle frame exhibited enhanced cellular uptake capability, as compared with flexible 2D DNA structures. In addition, the translocation of released DOX into the nucleus was proved by fluorescence microscopy, in which a DOX-loaded 3D DNA triangle frame displayed a stronger accumulation of DOX in nuclei. Moreover, given the facile drug loading and auto fluorescence of the anti-cancer drug, DOX, our results suggest that the DNA nanostructure is a promising candidate, as a label-free nanocarrier, for DOX delivery, with great potential for anticancer therapy as well.

COLL 795

Ultra-violet photoelectron spectroscopy studies on HOPG exfoliations in ambient air and ultra-high vacuum

Muhammad Salim¹, *mgs28@pitt.edu*, **Michelle Montgomery**¹, **Haitao Liu**². (1) Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, United States (2) Dept of Chem, Eberly HI 201, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

We report the surface chemistry of highly ordered pyrolytic graphite (HOPG) upon exposure to ambient air, as analyzed using Ultra-Violet Photoelectron Spectroscopy (UPS). UPS measurements were collected from freshly-cleaved HOPG in ultra-high vacuum (UHV) and after exposures to ambient air. We observed an immediate contamination of freshly-cleaved HOPG surface upon exfoliation in ambient air, followed by further growth and changing composition during longer air exposures. The advantage of UPS over XPS in the surface analysis of carbon substrates is highlighted and used for contamination characterization.



COLL 796

Inverse electron demand Diels-Alder reaction for surface modification of sp^2 hybridized carbon nanomaterials

Jun Zhu, jun.zhu@mcgill.ca, R Bruce Lennox. Chemistry, McGill University, Montreal, Quebec, Canada

Carbon nanotubes, graphite, and graphene have a number of fascinating electric, thermal, and mechanical properties. However, their applications often require physical adsorption or covalent attachment of chemical entities. Covalent chemical modification method is desired due to the high stability of the resulting modified carbon nanomaterials, but is particularly challenging due to the limited reactivity of the extended conjugated pi-system. We have thus applied the inverse electron demand Diels-Alder reaction (IEDDA) to the modification of single-wall carbon nanotubes (SWCNT) and highly ordered pyrolytic graphite (HOPG). Tetrazine-derivatized molecules or tetrazine-capped metal nanoparticle/nanorods are shown to react with these sp^2 hybridized carbon nanomaterials under ambient conditions. Site-specific modification is also achieved using tetrazine derivatives as the “ink” for microcontact printing.

COLL 797

Applying imaging XPS towards understanding surface phenomena of 2D-like and nano-material structures

Justin M. Gorham¹, justin.gorham@nist.gov, William A. Osborn¹, Jeremiah Woodcock¹, Keana C. Scott¹, John M. Heddleston², Angela R. Hight Walker², Jeffrey Gilman¹, Frank DelRio¹, Moh R. Amer^{4,5}, Abdullah Alrasheed⁴, Sarah A. Alodan⁴, Koo-Hyun Chung⁶. (1) MML/MMSD, National Institute of Standards and Technology, Frederick, Maryland, United States (2) Physical Measurement Laboratory, NIST, Gaithersburg, Maryland, United States (4) Center of Excellence for Green Nanotechnologies, King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia (5) Dept of Electrical Engineering, UCLA, Los Angeles, California, United States (6) School of Mechanical Engineering, University of Ulsan, Ulsan, Korea (the Democratic People's Republic of)

Traditional X-ray photoelectron spectroscopy (XPS) is considered one of the workhorse instruments of many research facilities focusing on surface chemical analysis. This tool typically generates spectroscopic data on surface composition and chemistry from areas defined by spot sizes 100's of micrometers in diameter to many millimeters. Perhaps a less employed tool is imaging mode XPS (iXPS), which has a much higher spatial resolution of 3 μm – 5 μm . Spectroscopy can be extracted from stacks of images, albeit at the expense energy resolution. Recent work in our laboratories has focused on employing iXPS to better understand chemical phenomena at the surface of materials that are localized to 10's of micrometers or less. The focus of the presentation will be two-fold. The first section will involve discussing challenges associated with

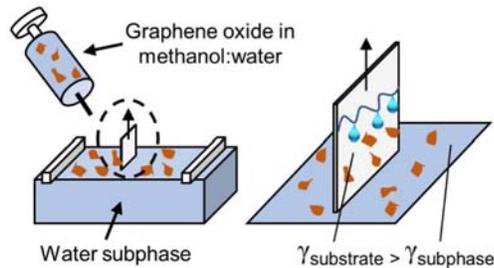
applying the iXPS, including development of tools to manipulate the large hyperspectral image stacks generated by the technique and addressing phenomena such as mechanically and magnetically induced drift. In the second section, we will discuss some recent successes that we have had applying iXPS to three different questions which required enhanced spatial resolution *and* surface (top 10 nm or less) chemical analysis. These will include characterizing 1) dispersion quality of MWCNT in a differentially charging carbon composite, 2) chemical transformations of MoS₂ before and after laser thinning, and 3) impact of heat treatments on black phosphorous's surface chemistry and optical properties.

COLL 798

Langmuir-Blodgett deposition of graphene oxide — identifying Marangoni flow as a process that fundamentally limits deposition control

Alexander Holm, aholm@stanford.edu, Cody J. Wrasman, Andrew R. Riscoe, Matteo Cargnello, Curtis W. Frank. Chemical Engineering, Stanford University, Stanford, California, United States

Langmuir-Blodgett deposition is a popular route to produce thin films of graphene oxide for applications such as transparent conductors and biosensors. Unfortunately, film morphologies vary from sample to sample, often with un-desirable characteristics such as folded sheets and patch-wise depositions. Often, differences in film morphologies are ascribed to differences in physical and chemical properties between graphene oxide samples. Here we propose that another process fundamentally limits control in Langmuir-Blodgett deposition of graphene oxide. Methanol is usually used in conventional Langmuir-Blodgett deposition to spread graphene oxide onto an air-water interface before deposition onto substrates. Here we show that methanol gives rise to the Marangoni effect which disrupts graphene oxide films during depositions. We directly showed the presence of Marangoni flow using photography, and we evaluated depositions with atomic force microscopy. The disruptive effect of Marangoni flow was demonstrated by comparing conventional Langmuir-Blodgett depositions to depositions where Marangoni flow was suppressed by addition of surfactant. Alcohol is ubiquitous as a spreading solvent for conventional Langmuir-Blodgett deposition of graphene oxide. Thus, the Marangoni effect is a general problem, and may explain the wide variety of un-desirable deposition morphologies observed in the literature. We are currently developing alternative methods for better control over graphene oxide thin film deposition. Promising results from this ongoing work will also be presented.



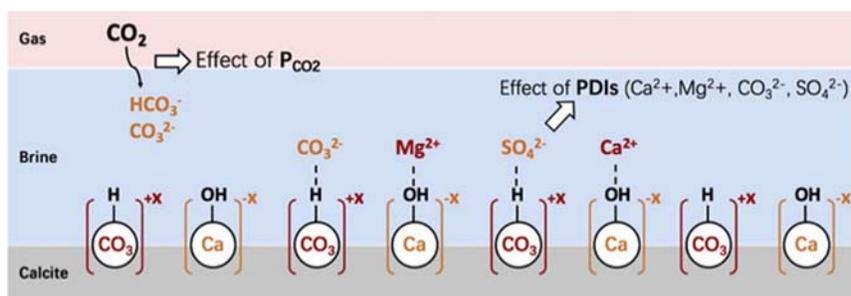
The methanol:water mixture present at the air/water interface in conventional LB deposition of graphene oxide gives rise to a surface tension gradient ($\gamma_{\text{substrate}} > \gamma_{\text{subphase}}$) which leads to Marangoni flow that limits deposition control.

COLL 799

Surface complexation modeling of calcite zeta potential in mixed brines with varied ionic strength for carbonate wettability characterization

Jin Song¹, js110@rice.edu, **Yongchao Zeng**¹, **Xindi Duan**¹, **Maura Puerto**¹, **George J. Hirasaki**², **Sibani L. Biswal**³. (1) Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States (2) Rice Univ Chem Engr Dept, Houston, Texas, United States (3) Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States

We presents zeta potential measurements and surface complexation modeling (SCM) of synthetic calcite in various conditions (brine ionic strength, ionic composition, CO₂ partial pressure). The systematic zeta potential measurement and the proposed SCM provide insight into the roles of four potential determining ions (Mg²⁺, SO₄²⁻, Ca²⁺ and CO₃²⁻) in calcite surface charge formation and facilitate the revealing of calcite wettability alteration induced by brines with designed ionic composition (“smart water”). In this work, the calcite zeta potential is measured in various brines (Ionic strength from 0.001M to 0.5M) under two different CO₂ partial pressure (10^{-3.4}atm and 1atm). Then, a SCM is developed to fit all the zeta potential. After showing our model can accurately predict calcite zeta potential in brines containing mixed PDIs, we apply it to predict zeta potential in ultra-low and pressurized CO₂ environments for potential applications in carbonate enhanced oil recovery including miscible CO₂ flooding and CO₂ sequestration in carbonate reservoirs. Model prediction reveals that pure calcite surface will be positively charged in all investigated brines in pressurized CO₂ environment (>1atm). Moreover, the zeta potential of several natural carbonates is measured and compared with the synthetic calcite’s result to investigate the effect of surface impurities, which is shown to significantly lower the carbonate zeta potential.



COLL 800

Molecular and dissociative adsorption of DMMP, Sarin and Soman on dry and wet $\text{TiO}_2(110)$ using density functional theory

Yenny P. Cardona-Quintero, *yenny.p.cardonaquintero.ctr@mail.mil*, Ramanathan Nagarajan. Natick Soldier RDEC, Natick, Massachusetts, United States

Titania, among the metal oxides, has shown promising characteristics for the adsorption and decontamination of chemical warfare nerve agents, due to its high stability and rapid decomposition rates. In this study, the adsorption energy and geometry of the nerve agents Sarin and Soman, and their simulant dimethyl methyl phosphonate (DMMP) on TiO_2 rutile (110) surface were calculated using density functional theory. The molecular and dissociative adsorption of the agents and simulant on dry as well as wet metal oxide surfaces were considered. For the wet system, computations were done for the cases of both molecularly adsorbed water (hydrated conformation) and dissociatively adsorbed water (hydroxylated conformation). DFT calculations show that dissociative adsorption of the agents and simulant is preferred over molecular adsorption for both dry and wet TiO_2 . The dissociative adsorption on hydrated TiO_2 shows higher stability among the different configurations considered. The dissociative structure of DMMP on hydrated TiO_2 (the most stable one) was identified as the dissociation of a methyl group and its adsorption on the TiO_2 surface. For the nerve agents Sarin and Soman on hydrated TiO_2 the dissociative structure was by the dissociation of the F atom from the molecule and its interaction with a Ti atom from the surface, which could indicate a reduction in the toxicity of the products. This study shows the relevance of water adsorption on the metal oxide surface for the stability and dissociation of the simulant DMMP and the nerve agents Sarin and Soman on TiO_2 .

COLL 801

Adsorption of high molecular weight polymers on clay surfaces

Carol E. Mohler¹, *cemohler@dow.com*, Michael Poindexter¹, Greg Meyers¹, Carl Reinhardt¹, Alan I. Nakatani². (1) Dow Chemical Company, Midland, Michigan, United States (2) Analytical Sciences, The Dow Chemical Company, Lansdale, Pennsylvania, United States

Understanding the adsorption of polymers on inorganic surfaces is critical in a variety of industrial applications including water treatment, pigmented architectural coating formulations, cement formulations, and pulp and paper manufacture. For example, the removal of inorganic solids during water treatment is typically accomplished using high molecular weight polymeric flocculants, which are thought to remove clay particles by a bridging flocculation mechanism. However flocculation is a complex phenomenon affected by multiple variables such as clay species and surface charge, clay content, particle size, pH, polymer charge, and mixing conditions. This paper describes the use of surface-sensitive methods such as atomic force microscopy, quartz crystal microbalance and small angle neutron scattering to provide insight into the interactions of model clay particles with high molecular weight polymers, and the morphology of the adsorbed polymer on the clay surface. Unique high-throughput imaging methods are also leveraged to describe the clay settling rates using different flocculants.

COLL 802

Vibrational SFG of thermally treated clay minerals

Ariel E. Nessl¹, pilotav07@gmail.com, Angelo Montenegro¹, Erica Howard¹, Muhammet Mammetskulyev¹, Brent C. Melot², Alexander V. Benderskii². (1) Chemistry, University of Southern California, Los Angeles, California, United States (2) Department of Chemistry, University of Southern California, Los Angeles, California, United States

Clay minerals are layered structures with large surface areas. Their adsorption and intercalation properties make them ideal candidates for environmental remediation through removal of pollutants from aqueous environments. Thermal modifications to nickel phyllosilicates induce defects, such as deprotonation, which changes the adsorption and intercalation properties. In order to understand how the properties have changed, we must first understand what the thermal treatment has changed on the surface. FTIR studies show the primary change is a splitting of the hydroxyl stretching peak. Vibrational SFG of the nickel phyllosilicate and the thermally treated nickel phyllosilicate resolved the hydroxyl stretching peaks seen in FTIR, showing two distinct peaks. Orientational studies indicate a significant difference in the orientation of the two hydroxyl moieties before and after thermal treatment. Compared to other techniques, SFG allows us to study the orientation of the hydroxyls at the interface, as opposed to bulk measurements previously done with clay minerals, such as neutron scattering and XRD. This technique identified the modified surface site and can be applied to in situ studies of adsorption.