

COLL 1

Virus Particle-Based Materials: Engineering and Biological Activity

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Virus-like particles (VLPs) are easily modified by chemical and biological means, retaining excellent properties of stability and structural homogeneity. We have explored the bacteriophage Q-beta capsid as a prototypical VLP for the development of biologically-active entities and assemblies. The synthesis of polymer- and carbohydrate-decorated particles will be described, along with the characterization of their physical, circulatory, and immunological properties relevant to the development of vaccines and diagnostic agents.

COLL 2

Cowpea mosaic virus and virus-like particles for material synthesis

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Biological nanoscience sits at the interface between chemical, biological and material sciences. The properties of plant virus particles make them useful synthons, scaffolds and templates for applications in bionanoscience. Adaptation of the virus particles facilitates their use as platforms for multivalent presentation of ligands and as templates for materials synthesis. For example, *Cowpea mosaic virus* (CPMV) particles are ca. 30 nm diameter icosahedra with well characterised physical, genetic and biological properties; they are preformed, pseudo-spherical, monodisperse nanoparticles. The properties of CPMV make it a natural, robust, nanoscale building block for inorganic materials synthesis and for the development of targeted carriers of therapeutic agents. Further, it has been shown that empty CPMV-based virus-like particles, that contain no genomic nucleic acid, can be used in the synthesis of encapsulated inorganic materials and for internal loading. The virus-based nanomaterials have potential applications in, for example, sensors, diagnostics, therapeutics and catalysis.

COLL 3

Plant virus-based nanostructures at the interface of materials science and biology

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A quintessential key in nanotechnology and materials science is to self-assemble multifunctional nanoparticles with well-defined properties. Nature has already perfected the self-assembly of various nanostructured molecules and materials. We have turned toward the structures of plant viruses (termed viral nanoparticles, VNPs). These highly symmetrical nanomaterials come in various shapes and sizes, but each species is highly monodisperse. VNPs have a high degree of symmetry and polyvalency. These features render VNPs attractive carrier systems for medical applications. Genetic and chemical engineering can be applied to introduce hundreds to thousands of copies of targeting ligands, therapeutics and imaging moieties. Functionalities can be introduced at the exterior and interior surfaces, and with spatial control. In this presentation, I will highlight the application of engineered VNPs for tissue-specific imaging and drug delivery. Specifically, I will introduce our recent work, which focuses on the study of structure-function relationship studying VNPs of different shapes in *in vivo* mouse models. Further, I will outline methods for the development of hierarchically organized VNP-networks and their applications in medicine.

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COLL 4

Constrained atom transfer radical polymerization within the capsid of the bacteriophage P22

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Capsids derived from the bacteriophage P22 are robust and versatile nanoplateforms. Two distinct interfaces (exterior and interior) of these hollow, spherical nanocontainers allow for encapsulation of cargo and targeted delivery to desired tissues. To encapsulate high payloads of small molecule cargos, we have utilized atom transfer radical polymerization (ATRP) to incorporate a cross-linked polymer network consisting of poly(2-aminoethyl methacrylate) (AEMA) monomers constrained to the inside of the P22 capsids. The AEMA can subsequently be derivatized with small molecules to achieve very high loading of the capsid. For applications in magnetic resonance imaging (MRI), we have attached 10,000 Gd per capsid, corresponding to an internal concentration of 150 mM Gd. At 60MHz (1.4T), this protein-polymer hybrid demonstrated ionic relaxivities (r_1) of $22.0 \text{ mM}^{-1}\text{s}^{-1}$, and an extremely high per particle

relaxivity of $200,000\text{mM}^{-1}\text{s}^{-1}$, placing these constructs comfortably in the upper end of observed macromolecular relaxivities.

COLL 5

Packaging nanoparticles into enveloped virus-like particles

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Viral particles are transport vesicles that have the potential to deliver different cargo to specific targets. Plant and bacteria viruses are good platforms for chemical modification and encapsidate a wide range of cargo; however, these viruses do not usually target human cells. Oncolytic animal viruses are able to discriminate between human target and non-target cells but can only be modified at the genetic level, thus minimizing the range of cargo being delivered. Our lab has developed a method to incorporate a range of cargo (nucleic acids, small molecules, and nanoparticles) into an enveloped oncolytic virus, having the advantages of both the plant and animal virus systems. The viral nanoparticles we have developed may potentially provide the balance needed for designing viral particles for diagnostic, therapeutic, and biomedical applications in medicine as well for exploring fundamental cell processes.

COLL 6

RNA-guided self-assembly of nanotube architectures: Growing plant viral sprouts and brushes on solid substrates

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Tobacco mosaic virus derivatives with multivalent, biochemically addressable protein surfaces are promising tube-shaped nanocarriers for capturing, catalytic, signal-generating and -transducing (biogenic or inorganic) moieties. Not only can the >2,100 coat protein (CP) subunits per virion be tailored genetically to support distinct coupling reactions, but also can the nucleoprotein helix be assembled *in vitro* from heterologous RNA constructs and CP types. This allows to modulate the nanoarchitectures' composition, length and shape up to 'nanoboomerangs' and 'trees'. 3'-terminally immobilized RNA controlled a site-selective bottom-up fabrication of tube arrays on demand, on Si wafers, polymers and metal colloids (then 'nanostars'). The hybrid structures are promising candidates for a high-density presentation of molecules in 'systems-on-a-chip' or 'liquid arrays'. Close-to-application tests point at immense capacities to act at interfaces with physical and (bio)chemical environments. These include stabilized ferrofluids, biotemplated transistor components, and 3D-scaffolded

fluorophores and enzymes expected to operate complex technical, catalytic or diagnostic processes.

COLL 7

Nature of target lipid influences outcomes of interfacial activity of amphipathic peptides

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World-wide an increase in pathogenic bacteria that are (multi-)resistant to commercially available antibiotics has been observed, while the number of effective antibiotics has declined steadily. One promising strategy to combat such pathogens is based on cationic host defense peptides, which can discriminate between bacterial and mammalian cell membranes interacting predominantly with negatively charged lipids exposed on the bacterial cell membrane surface.

Moreover, the amphipathic nature of these peptides confers them interfacial activity as can be deduced from stable monolayers at the air-water interface. Insertion of the peptides into the bilayer disrupts the lipid packing altering the lateral lipid pressure profile, which results in diverse effects on membrane structure and integrity depending on headgroup charge and hydrocarbon chain length of the membrane lipid. For example, peptides that tend to reside in the bilayer interface owing to their amphipathic moment along the helical axes induce at high concentrations as function of the target lipid either interdigitated membrane structures or micellization.

COLL 8

Structural and thermodynamic characteristics of melittin-phospholipid bilayer interaction: Results from computer simulations

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We performed molecular dynamics computer simulations where we used different level of detail in the description of force fields: from all-atoms to simplest models, to study the structural properties of melittin peptide when it was adsorbed on a lipid bilayer surface or when it was in a transmembrane conformation. We also studied the structural properties of the assembly of peptides and the effect of such an assembly on the membrane pore creation mechanism. While simulations using all-atoms force field allowed us to obtain estimates for the free energy of adsorption and free energies of transition from the surface to the transmembrane states, the simulations that employed less detailed force fields and therefore performed over longer time periods, provided us

with information on the character of the bilayer disruption due to the presence of peptides. Combining all-atoms and coarse-grained simulations results we were able to propose a possible mechanism of melittin action on lipid bilayers, consistent with some recent experimental observations.

COLL 9

Discovering highly potent pore-forming peptides using synthetic molecular evolution

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There are many natural and designed peptides that permeabilize membranes, and there are multiple mechanisms by which membrane permeabilization can occur. Yet, peptides that unequivocally self-assemble into equilibrium, membrane-spanning pores at low peptide to lipid ratios (P:L£1:1000) are very rare. The design and engineering of such peptide “nanopores” in lipid bilayer membranes is desirable as it could lead to improved biosensor platforms, targeted therapeutics, exogenous ion channels, or drug delivery vehicles. While the few well studied pore-forming peptides have provided a lot of information about the architecture of peptide pores, especially α -helical pores, our knowledge of the fundamental molecular principles of pore formation is not detailed enough for rational engineering. This is a roadblock to the design of new pore-forming peptides and to the optimization of known pore-formers for particular applications. In this work we show how novel, highly potent, equilibrium pore-forming peptides can be discovered using synthetic molecular evolution, i.e. iterative cycles of combinatorial library design and high-throughput screening. In the first example, we used two generations of *de novo* library design and screening to identify highly potent pore-formers that self-assemble into β -sheets in membranes. These peptides may be the only known examples of highly potent, pore-forming peptides that have β -sheet secondary structure in membranes. In the second example we designed an iterative library that used the helical pore-former melittin as a template. From this library we identified gain-of-function pore-formers that are much more potent than melittin. The results demonstrate the power of synthetic molecular evolution for the discovery and engineering of membrane active peptides.

COLL 10

Aminoacylated Phospholipids and Their Impact on the Interactions of Antimicrobial Peptides with Phospholipid Vesicles

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Aminoacylated phosphatidylglycerols (PG) are common lipids in the cytoplasmic membranes of Gram-positive bacteria. Their presence in staphylococcal membranes has been linked to increased resistance to a number of antibacterial agents, including antimicrobial peptides. Most commonly, the PG headgroup is esterified to lysine, which converts anionic PG into a cationic lipid with a considerably increased headgroup size. We have been studying how the presence of aminoacylated lipids in lipid vesicles affects the activity of two antimicrobial peptides, cecropin A and mastoparan X. To differentiate between the effects of headgroup charge and size on peptide-lipid interactions, we synthesized two different derivatives. In one, the headgroup was modified by the addition of lysine, and in the other, by glutamine. We find that the aminoacylated lipids can drastically inhibit the release of content from lipid vesicles to a degree that depends on the mode-of-action of the peptide studied.

COLL 11

Antimicrobial peptide arrays for discriminatory endotoxin sensing: understanding ligand and analyte interfacial chemistries

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Interfacially active antimicrobial peptides (AMPs) have received significant attention for uses ranging from therapeutics to active agents in antibacterial surfaces. In addition to use as antimicrobial agents, AMPs have potential as sensing agents with many advantageous properties superior to the ubiquitous antibody-based biosensors. Utilizing small arrays of naturally occurring AMPs, we have shown discriminatory binding of the immobilized AMPs to lipopolysaccharide (LPS, sepsis agent) molecules from different bacterial species, strains, and serotypes. Furthermore, we demonstrate differential binding of LPS molecules from bacteria grown under different environmental conditions. To elucidate the nature of LPS-AMP binding selectivity, both natural and rationally designed AMP sequences were utilized to systematically investigate the effects of key interfacial properties including charge, hydrophobicity, and amphiphilicity. Our results show the influence of both overall charge and hydrophobicity, but more importantly the spatial distribution and location of these properties relative to the peptide-substrate interface on AMP-LPS binding selectivity.

COLL 12

Fast evaluation and screening of anti-microbial peptide (AMP) activity by potential mean force MD simulations

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The widespread use of antibiotics has promoted the growing threat of bacteria that are resistant to almost all available antibiotics. Antimicrobial peptides (AMPs) represent a promising generation of antibiotics because they have broad-spectrum activity and lower toxicity. However, due to the limited sequence diversity of AMPs, it is challenging to identify and design new potent AMPs by quickly and accurately evaluating their antimicrobial activity. In this work, we develop potential-mean-force (PMF) coarse-grained molecular dynamics simulations to measure the free energy required to transfer the peptides from bulk water phase to water-membrane interface to bilayer interior. The PMF results reveal that different PMF shapes can indeed identify different membrane insertion scenarios by mapping out peptide-lipid energy landscapes during peptide insertion. Antimicrobial activity appears to be closely related to the transmembrane ability. The PMF profile can be an instructive index to distinguish and identify antimicrobial activity of designed and existing AMPs.

COLL 13

Selectively shaping noble metal nanocrystals by using electrostatic potential surface of small molecule as a guide

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We demonstrate the electrostatic potential surface can be used as guidelines to predict the facet binding selectivity of small molecules to Pt and Pd. Aromatic compounds with negative electrostatic potential surface in the ring system showing binding specificity to Pt {111} facets are used to synthesize Pt nano-tetrahedra. The binding affinity is also related to the relationship between molecular binding sites and Pt atoms. Raman spectroscopy was used to investigate their binding configurations that benzene ring of aromatic compound with Pt {111} facet binding specificity adsorbs parallel to Pt (111) surface. Small molecules with a positive electrostatic potential surface show a potential binding preference to Pt {100} facets. We rationally selected small molecule to synthesize Pt nanocubes as design. At last, we demonstrate the guidelines in another materials system, i.e., Pd. Our study represents a significant step toward the development in predictable and programmable materials synthesis through design.

COLL 14

I-motif-mediated synthesis of Pd nanocatalysts

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Biotemplating on the basis of DNA self-assembly has been considered as an attractive method to produce metal nanomaterials. However, the mechanism how biomolecular

templates affect the size, morphology and physicochemical properties of metal nanoparticle is far from clarity. We develop a facile approach to synthesize Pd nanoclusters with high catalytic activity towards the reduction of 4-nitrophenol using the DNA template adopting i-motif structures. Experimental characterization and DFT calculations disclose that the unique structure of i-motif can provide spacial constraints for the growth of Pd nanocluster and highly dispersed Pd adatoms involving one-atom or double-atom Pd can be generated at low [Pd]/[base] ratio. More intriguingly, the Pd-base interactions facilitate the activation of 4-nitrophenol so that the catalytic activity of Pd nanoclusters is extremely high. This work suggests a promising pathway to modulate physicochemical properties of metal nanomaterials with precision adjustment of the nucleation and growth mode of nanoclusters.

COLL 15

Morphology modulation of Cu₂O film via novel hydrothermal redox approach: The significant influence of anionic groups

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Cu₂O has attracted much attention in photocatalysis and photoelectrochemical (PEC) water splitting. In this work, a simple hydrothermal approach is developed to prepare Cu₂O film *via* the redox reaction between Cu²⁺ and Cu plate. Simply tuning the anionic groups of Cu²⁺ can effectively modulate the morphology of rod arrays, cross-linked and truncated octahedrals, respectively. The characterizations indicate that the novel rod arrays have more copper vacancies and higher optical absorption than the other two morphologies, owing to its network structure and abundant edges and corners. As a result, the rod arrays exhibit much better performance in PEC and photodegradation tests. Interestingly, the photostability of the three morphologies is distinct and morphology-dependent. In PEC test, Cu₂O films suffer from photoreduction, especially for rod arrays. However, in the photodegradation, the rod arrays show high stability, accompanied with surface reconstruction that benefits the charge separation. For cross-linked octahedral and truncated octahedral, the electron and hole dominate the photodegradation while the extra counterparties cause the oxidation and reduction of Cu₂O, respectively.

COLL 16

Surface Chemistry on ITO surface via Piers-Rubinsztajn reaction

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Previously, we demonstrated that the condensation of aryloxybenzene derivatives with hydrosilanes, catalyzed by $B(C_6F_5)_3$, leads to silicone-modified aromatics. We now demonstrate, surprisingly in light of the size of the catalyst, that the reaction can also be induced on the surface of ITO.

ITO surfaces were first modified with a hydrosilane coupling agent using traditional methods. Exposure of the ITO surface to the arylamine in the presence of low quantities of $B(C_6F_5)_3$ led to a surface to which was tethered the amine. A combination of CA, SEM and AFM images demonstrated the modification had occurred. In addition, AFM also demonstrated the presence of particles chemisorbed on the surface ranging in size from about 20-40 nm in diameter. EDX analysis of the well-defined organic nanoparticles confirmed the presence of nitrogen, thereby indicating amines.

The potential of these materials to affect electron transport in the region of the ITO interface will be discussed.

COLL 17

Dramatic promotion of water-mediated effects on surface adsorption modulation and dye sensitization of TiO_2

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Solar-light-induced photosensitization has drawn much attention in environmental remediation and solar cells. Dye adsorption on TiO_2 is the prerequisite for electron transfer, which determines the photocatalytic efficiency. Dye molecules are excited by solar light, and then inject electron into the conduction band of TiO_2 . Our work shows that water pre-bonded to the surface bridging hydroxyls of TiO_2 can modulate the surface electronic structure via polarization, change the adsorption mode of cationic dye from common mode ($Et_2N=R_nCOO\cdots Ti$) to electrostatic adsorption ($R_n=N^+Et_2\cdots O_{br}^-$). This novel adsorption mode is highly efficient for electron transfer from dye to TiO_2 . As a result, simply stirring P-25 in water promotes the photodegradation rate by 5 times. We further prepared hierarchical TiO_2 with macro/mesoporous structure, and its photodegradation rate is increased more than 4 times compared with P-25. This result opens a door towards facile improving the efficiency of dye-sensitized applications for environmental remediation and solar cell.

COLL 18

TiO_2 : Adsorption and photochemical activation of molecular oxygen

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TiO₂ has received widespread attention as a basis both for solar energy collection and for environmental remediation. In both applications, the wide band gap and low efficiency limit effectiveness. This contribution reports results of combining ultra-nano particles (< 2nm) with iron doping. The combination modifies TiO₂ electronic states, efficiently activating molecular oxygen and altering the photo-oxidation mechanism to become a catalyst-mediated, charge transfer reaction. The altered mechanism arises due to surface adsorbed, molecular oxygen associated with an iron-induced interband state. In the absence of iron, TiO₂ either reduces water or stores the electron; with iron *and* molecular oxygen pollutants are photo oxidized with nearly three times the efficiency of undoped TiO₂. In the absence of molecular oxygen, charge transfer is quenched.

COLL 19

Photochemical renoxification of nitric acid on real urban grime

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In recent years there has been increasing interest in understanding the formation of pollutant films on impervious surfaces exposed to the atmosphere and their role in influencing atmospheric processes. Often referred to as urban grime, these films sequester compounds such as polycyclic aromatic hydrocarbons (PAHs), and halogenated aromatics (ie. PCBs) as well as inorganic compounds such as nitrates and sulfates from the gas phase. Films are also thought to facilitate heterogeneous chemistry such as PAH ozonation as well as photochemistry such as the possible photochemical production of NO_x and OH important species for air quality determination. This suggests that these films may play a role in altering atmospheric composition especially in urban environments. In order to explore photochemistry on the films, Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) has been used to track changes in chemical composition of grime following illumination. Authentic urban grime is grown directly on ATR crystals by exposing them to the atmosphere in downtown Toronto, allowing for the films to be studied without the necessity of extraction techniques used in previous studies. Monitoring the change in composition of the film on the crystal during illumination with a solar simulator, showed the photo removal of nitrate from grime. We will present results comparing the photochemistry of authentic grime with proxy films as well as aqueous nitrate photochemistry showing evidence of a possible mechanism for a fast renoxification pathway for HNO₃.

COLL 20

Insights into the Chemical and Photochemical Mysteries of O₂ on Rutile TiO₂(110)

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Molecular oxygen is a reactant or product in many important catalytic and photocatalytic processes occurring on oxide surfaces, with obvious examples including water splitting and partial oxidation. Oxygen is also commonly used as a processing gas in the preparation of catalysts, ceramics and other important materials, and has obvious importance in many environmental settings. Using the rutile $\text{TiO}_2(110)$ surface as a prototype, this talk will illustrate how the field's understanding of the interactions of oxygen with oxide surfaces has evolved and deepened over the last two decades. The presentation will provide a historical look at the interaction of oxygen with vacancy sites on $\text{TiO}_2(110)$, and then focus on recently obtained insights into the roles of O_2 in photooxidation reactions, highlighting the complexities of its interactions with surface defects, photoexcited charge carriers and coadsorbates.

COLL 21

Ultra-thin oxide films as designable model catalysts

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In our group silica thin film systems have been designed and studied during the last decade and more. The goal was to use such films as model supports. Monolayer and Bilayer silica films have been successfully prepared. In fact, the bilayer SiO_2 film could be imaged in both, crystalline and amorphous phase. The phase transmission is being studied.

Moreover, it has been possible to incorporate aluminium into the film leading to the formation of two-dimensional alumosilicates, i.e. zeolites with "infinite cavities". The incorporation of aluminium into the bilayer film follows Löwenstein's rule and we demonstrate the formation of bridging OH groups with high acidity. Experimental evidence using STM, FTIR, and XPS are given. This study paves the way for studies in surface science of zeolite surfaces.

COLL 22

CO Induced Adatom Sintering in a Model Catalyst: Pd/ Fe_3O_4

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The $\text{Fe}_3\text{O}_4(001)$ surface forms a $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction in which a subtle lattice distortion couples to subsurface charge and orbital order^{1,2}. Together, these effects create a strongly corrugated adsorption landscape on which isolated Au^3 , Pd, $\text{H}^{4,5}$ and Fe^6 atoms are stable to high temperatures (400 °C). This makes the $\text{Fe}_3\text{O}_4(001)$ an ideal system to study the potential for single atom catalysis under reaction conditions, as well as study related phenomena such as sintering. In this presentation we focus

primarily on the Pd/Fe₃O₄(001) system, using time lapse scanning tunneling microscopy data to follow CO induced sintering at the atomic scale. Mass transfer occurs through a Pd carbonyl species, formed via the skyhook effect. Interestingly, while CO exposure leads to sintering, hydroxyl groups stabilize single atoms.

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COLL 23

Structure of the TiO₂(110) interface with water

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Much attention has been focused on the surface science of titanium dioxide (TiO₂) due to its numerous scientific and industrial applications in photocatalysis, electrochemistry, active coatings, gas sensors. Among these studies, many have focused on the interaction of water and the model rutile (110) surface, due to the fundamental role of water in many of the present and potential applications of TiO₂. The vast majority of experimental and theoretical understanding of the adsorption behaviour of water on TiO₂(110) concerns gas phase adsorption in ultra-high vacuum (UHV) environments (<1x10⁻¹⁰ mbar). Recent work by our group has attempted to characterise the atomic scale structure and composition of the water interface with the 'standard' UHV prepared TiO₂(110) surface using STM, surface spectroscopy and surface diffraction techniques.

Slightly reduced TiO₂(110) samples prepared in UHV before immersion in liquid water at room temperature were found to exhibit a 2x1 overlayer in atomic scale STM. The 2x1 periodicity of the overlayer leads to the formation of phase domains approximately

300 Å² in size. Core and valence level photoelectron spectra show the overlayer is composed solely of OH. The structure of the water-TiO₂(110) interface was investigated by surface X-ray diffraction measurements for three environments: a dipped sample, a liquid cell, and an *in situ* vapour dose. The bestfit model for all three consists of an overlayer composed of hydroxyls bonded either atop Ti_{5c} or in bridging sites.

COLL 24

Surface Chemistry of the Rutile TiO₂(011)-2x1 Surface

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We investigate adsorption and reaction of hydrogen and acetic acid on the TiO₂(011) surface and compare it to results for the (110) surface results. In particular we show that diffusion of hydrogen into the bulk becomes favorable at elevated temperatures and this precedes lattice oxygen abstraction and water formation, which has been suggested for the (110) surface. For strongly covalent bonded molecules, like acetic acid, we propose a restructuring of the surface upon chemisorptions. Thermal reaction of acetate with the TiO₂ substrate results in oxidation of Ti-interstitials at the surface causing formation of a new TiO₂ surface phase. We end the talk by discussing the electronic properties of this new surface.

COLL 25

Hydrogen Interaction with Oxide Surfaces: Reduction and Hydroxylation

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The thermodynamically most stable structures and compositions of ZnO and TiO₂ surfaces in a hydrogen atmosphere as function of temperature and partial pressure have been determined using density-functional theory calculations. By homolytic hydrogen adsorption the surfaces are reduced, and the amount of surface hydroxylation controls the charge state of oxygen vacancies. It will be shown that limits for surface reduction exist which depend on the specific oxide surface. By heterolytic hydrogen adsorption, on the other hand, hydride anions are formed which may be stabilized in oxygen vacancies. High activation barriers guarantee long enough lifetimes of the hydride anions so that they might be available for reduction steps in chemical reactions, for example, methanol synthesis. Since hydride formation, surface reduction by homolytic hydrogen adsorption and re-oxidation of the surface in chemical reactions are closely coupled, an understanding of the thermodynamic and kinetic stability of the reduction states of the oxide surfaces is essential for obtaining further insights into underlying reaction mechanisms.

COLL 26

Exploring electron-hole pairs in transition-metal oxides: a theoretical perspective

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Oxides are important materials for solar energy conversion and photo-catalysis. For a detailed understanding of their properties, insight from theory is crucial. This, in turn, requires a reliable description of optical excitations and the underlying electronic structure. Here, *ab initio* results turned out to sensitively depend on details of the used method as well as structural conformation. With density-functional theory (DFT) as a starting point we apply many-body perturbation theory in terms of the G_0W_0 approach as well as the Bethe-Salpeter equation, to describe for selected oxides the quasi-particle band structure and excitonic spectra, respectively. We explore the impact of crystal structure and relaxation effects as well as the choice of the specific approach together with the exchange-correlation potential on the characteristics of the electron-hole pairs.

Work in collaboration with Olga Turkina, Andris Gulans, Dmitrii Nabok (all HU Berlin), and Cristiana di Valentin (University of Milan)

COLL 27

Oxide Surfaces in the Light of Highly Brilliant X-rays

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The atomic structure of basic oxide surfaces was a secret for many years due to their insulating nature, which made them inaccessible for electron based techniques such as low energy electron diffraction or scanning tunneling microscopy. The intrinsic tendency of oxide surfaces towards charging was overcome using surface x-ray diffraction, which developed into a powerful oxide surface crystallography tool with the advent of hard x-ray synchrotron radiation. In my presentation I will review surface x-ray diffraction studies on surfaces of prototypical oxides such as $Al_2O_3(0001)$, $MgO(100)$ and $TiO_2(110)$, providing detailed structural information [1]. Further on, I will demonstrate, how surface x-ray diffraction helped to clarify the stabilization and reconstruction mechanisms of polar oxide surfaces such as $NiO(111)$ and $MgO(111)$, an important topic in oxide surface research [2]. As unique in-situ tool, surface x-ray diffraction can be employed to study oxide surfaces as a function of the oxygen chemical potential over a wide pressure range from ultrahigh vacuum to 1 bar and a wide temperature range, coupling the surface energetics to the surrounding gas atmosphere [2]. This makes a direct comparison with *ab-initio* thermodynamics density functional theory calculations possible, delivering complementary information on surface structure, composition and stability. In the case of oxides with reduced charging such as TiO_2 , scanning tunneling

microscopy can deliver additional information, helping to disentangle the correct structural model [3]. Surface x-ray diffraction is used today for the investigation of complex oxide surfaces such as SrTiO₃ and its interfaces to ultrathin insulating oxide films at which 2D electron gases are reported to form [4]. Recent results demonstrate that the use of anomalous surface x-ray diffraction can help in the case of multicomponent oxides to disentangle roughness from interdiffusion [5]. I will conclude in giving a perspective for future work on oxide surfaces using SXRD

COLL 28

Interaction of Gas Phase Molecules with Nanostructured Model Supported Catalysts: Thermodynamics and Kinetics

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Atomistic-level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. In our studies, we investigate kinetics and thermodynamics of heterogeneously catalyzed reactions and adsorption processes on nanostructured model supported catalysts to provide fundamental insights into the surface chemistry. By employing pulsed multi-molecular beam techniques, IRAS and synchrotron-based spectroscopies on Pd/Fe₃O₄/Pt(111) model surfaces, we investigate the mechanistic details of complex multi-pathway surface reactions, such as hydrocarbon transformation in presence of hydrogen or selective hydrogenation of multi-unsaturated hydrocarbons, to obtain the correlations between the reactivity, selectivity and the particular structure of the catalytic surface. Complementary, single crystal adsorption calorimetry is employed to address thermodynamics of adsorption processes and surface reactions, such as e.g. adsorption and reaction of oxygen and CO. Specifically, we focus on the particle size dependence of adsorption and reaction energies to obtain a fundamental-level understanding of how the nanometer scale confinement of matter effects the energetics of surface reactions.

COLL 29

Non-specific changes on surface of human cervical epithelial cells during cancer transformations

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Nonspecific (physical) changes of the cell surface of cells during transformation from normal to cancerous state are rather poorly studied. Here we describe our recent studies of such changes done on human cervical epithelial cells during their transformation from normal through infected with human papillomavirus type-16 (HPV-16), immortalized (precancerous), to cancerous cells. The changes were studied with

the help of atomic force microscopy (AFM) and through nonspecific adhesion of fluorescent silica beads to the cell surface. Based on the adhesion experiments, we clearly see the difference in nonspecific adhesion which occurs at the stage of immortalization of cells, precancerous cells. The analysis done with the help of AFM shows that the difference observed comes presumably from the alteration of the cellular “brush”, a layer that surrounds cells and which consists of mostly microvilli, microridges, and glycocalyx. Further AFM analysis reveals the emergence of fractal scaling behavior on the surface of cells when normal cells turn into cancerous. The possible causes and potential significance of these observations will be discussed.

COLL 30

Mechanical properties of breast cancer cells embedded in matrices

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Mechanical interactions between cells and the extracellular matrix (ECM) are critical to the metastasis of cancer cells. Along with the enhanced ability of metastatic cells to remodel ECM by catalyzing both degradation and cross-linking of ECM fibers, increased mechanical compliance confers these cells with a distinct advantage in reaching the other side. In the past several years, experimental perturbations of ECM stiffness *in vitro* have revealed the importance of 'outside-in' signaling in effecting cellular behavior and phenotype, and the physiological relevance of a 3D microenvironment has become increasingly clear. We have established a 3D model system investigating cell-ECM mechanics using an atomic force microscope (AFM) mounted on and synchronized with a confocal laser scanning microscope (CLSM). Along with the use of well-defined sphero-conical AFM probes with micrometer sized radii, the advancement of novel AFM indentation data analysis methods to correctly determine elastic moduli in a depth-dependent manner enables us to determine the stiffness of cells that are embedded in gels. Multi-color fluorescent labeling of the cell and ECM components, as well as the AFM probe, provides the detailed geometry of not only the cell and gel, but also of their contact with and deformation by the AFM tip during indentation, all of which are integral to the proper interpretation of force-indentation curves on such heterogeneous samples.

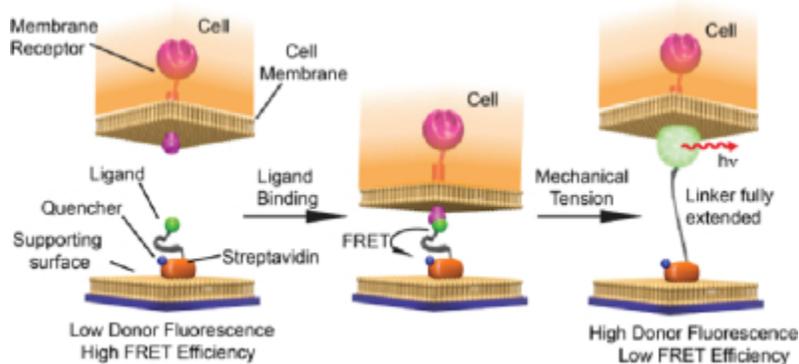
In this talk, we present results from experiments with collagen-embedded metastatic MDA-MB-231 breast cancer cells and immortalized non-tumorigenic MCF-10A mammary epithelial cells. Collagen I matrices ranging ~10-50 μm in thickness and ~100-10,000 Pa in elastic modulus are covalently attached to dishes. After polymerization, MDA-MB-231 and MCF-10A cells are seeded on the gels. The cells are given various amounts of time to adhere and/or invade the gel before fluorescent staining and combined mechanical/confocal measurements.

COLL 31

Biophysics at the Cell Surface: Developing probes to image tension applied by membrane receptors

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In this talk, I will describe our work that is focused on the synthesis and characterization of fluorescence-based turn-on probes for imaging the molecular tension across membrane receptors in real time (Stabley et al. Nature Methods 2012). All force gauges require two parts: a spring with a known force constant, and an accurate ruler. Likewise, our sensor takes advantage of fluorescence resonance energy transfer (FRET) between fluorophores as a molecular "ruler" and flexible polymer chain as a reversible entropic spring with a known spring constant. The sensor allows one to quantify molecular forces (1 –100 pN) with high spatial and temporal resolution for a wide range of membrane receptors and cell types. I will describe the application of these sensors to image forces associated with clathrin-mediated endocytosis, and integrin adhesion receptors. Given the superior optical and physical properties of gold nanoparticles, we have also developed second generation force sensors and these will be described in detail. Finally, I will discuss the development of chemical and enzymatic ligation strategies to generate recombinantly expressed tension probes.



COLL 32

RhoA-src crosstalk modulates cell stiffness and adhesion to the matrix

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Src is activated by mechanical stress and has an important role in the crosstalk with the RhoA pathway in regulating cell adhesion to the matrix. RhoA activation increases cell contraction by promoting actin polymerization and focal adhesion formation, hence increased cytoskeletal tension. To quantitatively investigate the relationship between adhesion strength and cell stiffness in the context of RhoA-Src crosstalk, force spectroscopy measurements using a fibronectin functionalized atomic force microscope probe were performed on cells expressing Src or RhoA mutants. While expression of constitutively active mutants for both Src and RhoA showed stronger adhesion to the matrix and an increase in cell stiffness, treatment with SU6656, a cell-permeable small molecule which inhibits Src kinase with high affinity, significantly reversed these effects. These results show that RhoA and Src crosstalk is not only important for cell adhesion, but there is a direct involvement of Src in cytoskeletal tension development.

COLL 33

Correlated imaging and force mapping on model membranes and cell surface markers

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Controlled surface chemistry will introduce molecular recognition and specificity. Integration with cell mechanics probed by AFM will bring new insights into cellular processes. Using self-assembly of block copolymer micelle loaded metal precursors, combined with a further seeding-growth route, a newly developed approach was demonstrated to create ordered gold nanoparticle (AuNP) arrays with a series of controllable sizes on almost any solid substrate. As an example, the optical response of AuNP arrays to local refractive indices can be characterized by the extinction spectra, and compared with theoretical simulations based on the AuNPs size, inter-particle spacing, and embedding ratio. AuNP arrays functionalized with lipid bilayers (cell membrane analog) and lipid binding proteins (cell surface marker analog) can be used to test our hypothesis that NP array enhanced sub-wavelength imaging may be obtained by p-TIRF. Quantitative evaluation and optimization are proposed to further explore the detection sensitivity of e.g., cancer cell surface markers.

COLL 34

Immunosensing with AFM

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Modern enzyme- (EIA/ELISA) and fluorescent- based (FIA) immunosensing assays allow for highly accurate, specific, and sensitive diagnostics. However, there is a need in lowering the limit of detection, higher sensitivity, and faster detection for prognosis and diagnosis of various health issues. Atomic force microscopy (AFM) is a natural instrument to study properties of biomolecules in their native environments. AFM has the ability of monitoring the assembly of the molecular layers in each step of preparation of immunosensors (can have up to five layers). Here we demonstrate the effectiveness of the AFM method to lower the limit of detection of DNF (a simulant of TNT) up to two orders of magnitude compared to the best results reported in the literature so far. In addition, AFM can be used to understand the limits of possible miniaturization of immunosensors. We demonstrate it as an example of sensing Antinitrotyrosine IgG and Antidinitrophenyl IgG by showing that the smallest size of immunosensors surface prepared according to the standard ELISA protocols can be as small as 3 square microns. This is about 4 million times smaller than the sensor surface currently used. Finally, we demonstrate that AFM can reliably distinguish complex immuno-signals (two antigens together versus the same antigens separately), which were impossible to resolve by using standard optical detection methods.

COLL 35

Accelerated SERS-based Immunoassays via Active Transport Through Gold Plated Filter Membranes

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The rate of mass transfer often limits the analysis time in conventional heterogeneous immunoassays. Previous works have demonstrated that active transport of the analyte to the surface immobilized antibody expedites antibody-antigen binding. In this work, we developed a porous gold filter membrane as a flow-through capture substrate to enhance antibody-antigen binding kinetics. The capture filter was incorporated into a surface-enhanced Raman scattering (SERS)-based immunoassay to demonstrate that we can significantly increase the assay speed without losing sensitivity by passing the sample and SERS labels through the capture filter using a syringe. A model antigen, mouse IgG, was used to establish proof-of-principle for the flow-through SERS-based immunoassay and to systematically investigate the effect of flow rate and pore size on antibody-antigen binding efficiency. Using the optimized capture filter and assay conditions, e.g., flow rates, an assay was developed for the detection of influenza virus.

COLL 36

Plasmon-Enhanced Enzymatic Reactions 3: Application to β -Galactosidase and Alkaline Phosphatase

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In this study, we describe the application of plasmon-enhanced enzymatic reactions (PEER) to two commonly used enzymes, i.e., β -galactosidase (β -Gal) and alkaline phosphatase (AP). Silver Island films (SIFs) were deposited onto 3-Aminopropyltriethoxysilane (APS)-coated glass slides at different loading (low, medium, and high) which were used as plasmonic surface. The immobilization of these enzymes onto SIFs was performed using (1) biotin-avidin protein assay and (2) biotin-poly (ethylene-glycol)-amine. Enzymatic activities were assessed using optical absorption spectroscopy. While an avidin assay enhancement was observed for AP on SIFs, no enhancement was observed for β -Gal due to potential inhibition of enzymatic activity. These results indicate that any enzymatic process that employs AP can be further enhanced by using SIFs.

COLL 37

The birth of a plasmon

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Information on the emergence of plasmons in noble metal nanoparticles is limited. This is primarily due to the challenge of preparing a series of molecularly precise clusters spanning a size range from small clusters to colloidal nanoparticles, but it is also due to the complex physical and chemical interactions between the metal core and surrounding media on optical excitations. Here, we overcome both of these challenges by recording a systematic series of spectra for discrete Ag magic-number clusters with different ligand shells. Spectra of the smallest clusters contained discrete superatom transitions that depended on the ligand but they evolved toward a single plasmonic peak, independent of ligand, for the largest particles. Surface-enhanced Raman scattering from $\text{Ag}_{44}(\text{p-MBA})_{30}$ clusters also showed that dipole transitions in superatom clusters are fundamentally similar to plasmonic excitations. A superatom description therefore emerges, describing plasmons as highly-degenerate single-electron excitations with very large transition dipole moments.

COLL 38

Effects of Nanostructure and Aggregating Agents on the SERS detection of Cotinine and trans-3-hydroxycotinine

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As the metabolites of nicotine, cotinine and trans-3-hydroxycotinine (3HC) have recently attracted more and more attention acting as the biomarkers. Here, various silver nanoparticles with different structure including pure spheres, Ag core-Au shell and silica core-Ag shell were synthesized and optimized to detect cotinine and 3HC using surface-enhanced Raman spectroscopy. In addition, the effect of various aggregating agents including five kinds of cations and three kinds of anions on the SERS detection was also investigated. Interestingly, the best aggregating agent to achieve maximum enhancement for the SERS detection depends not only on the analyte but also on the nanoparticles structure.

COLL 39

Selective Detection of Drugs using Molecular Imprinted Polymer Nanosensors

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Molecular imprinted polymer (MIP) integration into biosensors is becoming increasingly popular because of their improved stability and detection selectivity vs. traditional recognition agents. Herein, methacrylate-based aspirin, acetaminophen, and caffeine MIPs are synthesized, characterized, and used to selectively detect and quantify the amount of the drugs present in complex solution mixtures. First, polymerization occurs in the presence of aspirin, acetaminophen, or caffeine. Next, these template molecules are extracted thereby leaving a polymer with specific drug imprint sites. The imprinted MIPs are characterized using dynamic light scattering (DLS) and normal Raman spectroscopy. Finally, the materials are used for quantitative and selective drug detection using normal and surface-enhanced Raman scattering. We will demonstrate that integrating nanomaterials into the MIP sensor allows for the direct and selective detection of drug molecules in complex sample matrices. Better methods for detecting drugs in complex sample matrices is critical in achieving quantitative nanosensors.

COLL 40

Engineering silver and gold nanowires and nanoparticles for sensing applications

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Arrays of periodically disposed silver and gold nanowires grown in porous alumina can be post-fabricated to produce plasmonic devices that show intense SERS activity and useful properties such as plasmonic transport that allows one to excite one end of a nanowire bundle to detect molecules by SERS that reside at the opposite end, many microns away. Likewise, one can use a properly engineered DNA aptamer to link nanoparticles together and detect the SERS signal of multiple reporter molecules adsorbed on the nanoparticles resulting from the interaction of the aptamer with one or

two target molecules thereby amplifying the SERS effect and allowing a single analyte event to be routinely detected. The talk will illustrate such applications of gold and silver nanostructures.

COLL 41

Super-resolution imaging of plasmonic nanostructures

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Plasmonic nanostructures have attracted significant interest due to their ability to support surface-enhanced spectroscopies, such as surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF). This talk will describe recent efforts using super-resolution imaging to characterize interactions between plasmonic nanostructures and molecules on their surface undergoing either SERS or SEF.

COLL 42

Evaluation of SERS Au nanoparticles for triplexed labeling of B cell leukemia and lymphoma, and flow cytometry

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Surface-enhanced Raman scattering (SERS) gold nanoparticles are developed and characterized for imaging of cell surface receptors of interest in B cell leukemia and lymphoma. SERS nanoparticles are prepared by adsorbing various Raman-active dyes onto the surface of Au nanoparticles, and subsequently coating the particles with 5 kDa polyethylene glycol (PEG). The probes are targeted to cell surface proteins of interest using both research grade monoclonal antibodies and the therapeutic antibody, rituximab. Competitive binding experiments are used to investigate the specificity of the interaction between SERS particles and their surface protein targets. SERS labeling is compatible with fluorescence flow cytometry protocols and detection. Additionally, the particles' SERS is collected directly from labeled LY10 lymphoma cells using a flow cytometer. Three different SERS reporter probes are targeted to cell surface proteins simultaneously and triplexed SERS labeling is resolved using Raman maps derived from the results of least-squares fitting.

COLL 43

Halloysite nanotubes with controlled release of chemical agents for smart composites

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Natural halloysite clay nanotubes are described as 50 nm diameter and 1000 nm length containers for controlled release of chemical agents. Loading these tubes' 15-nm diameter lumens with chemicals, including bioactive molecules (self-healing, flame-retardant, anticorrosion, antimicrobial agents, proteins, DNA, and drugs) and doping them into polymers allows for a sustained release providing these nanocomposites with new smart properties. Typically, addition of 5-10 % halloysite synergistically increases materials strength on 30-70 %, 2-3 times enhances composite adhesivity and adds new functions due to triggered release of needed chemicals in defect points. The release may be enhanced by application of mechanical strength or by pH and temperature. Halloysite is biocompatible "green" material and its simple processing combined with low cost make it a perspective additive for polymeric composites.

COLL 44

Stimuli-Responsive Colloidal Nanoparticles and Nanotubes

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Materials with the ability of dimensional changes on demand exhibit many potential applications ranging from adaptive composites that mimic biological functions under extreme conditions to microfluidics or neural implants to stimulate components of the nervous systems. This seminar will outline our recent advances in the synthesis and assembly of colloidal nanoparticles and films that exhibit tunable color and shape responses. Ranging from nanoparticles consisting of variable shapes and on-demand color changes to tunable nanowires and cilia-like morphologies, this presentation will focus on physico-chemical aspects of colloidal dispersions as well as the development of thermally responsive biocompatible nanotubes engineered by *in-situ* assembly of biologically active phospholipids (PLs).

COLL 45

Cornell dots: Fluorescent core-shell silica nanoparticles to interrogate biological environments

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Fluorescent nanoparticles offer enormous scientific and technological promise as labels, photon sources and sensors for a range of biotechnological and nanomedicine

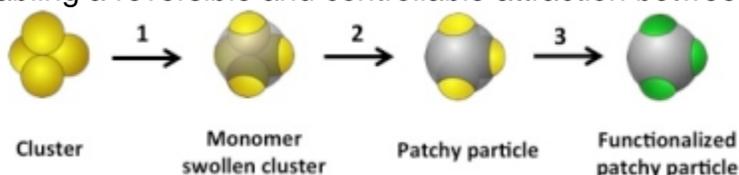
applications. Many applications require size-controlled, monodisperse, bright nanoparticles that can be specifically conjugated to biological macromolecules, targeted to specific environments, and remotely visualized. As an alternative to single molecule fluorophores and quantum dots, a novel class of multifunctional fluorescent silica-based core-shell nanoparticles referred to as “Cornell dots” or simply “C dots” hold particular promise since they are more biocompatible and are water soluble, and silica chemistry is well established and extremely versatile. The presentation will report on results on C dot synthesis, characterization and optical properties. Various life sciences applications are demonstrated with specific developments towards smaller than 10 nm sized PEGylated labels for nanomedicine, including the first dual-modality (optical/PET) hybrid nanoparticle of its class and properties receiving investigational new drug (IND) FDA approval for first in-human trials in the US.

COLL 46

Fabrication and Functionalization of Patchy Particles

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Patchy particles with well defined symmetries and specific interactions are desirable to construct micro-structured materials. We develop a method to fabricate particles with various numbers of patches, $n=1-7$ and higher, that adopt spherical, linear, triangular, tetrahedral, trigonal dipyramidal, octahedral or pentagonal dipyramidal symmetries. The patchy particles are formed from clusters using a two-stage swelling method followed by polymerization. Patches can also be site-specifically coated with oligonucleotides, enabling a reversible and controllable attraction between patches on different particles.



COLL 47

Colloids with valence: specific directional bonding

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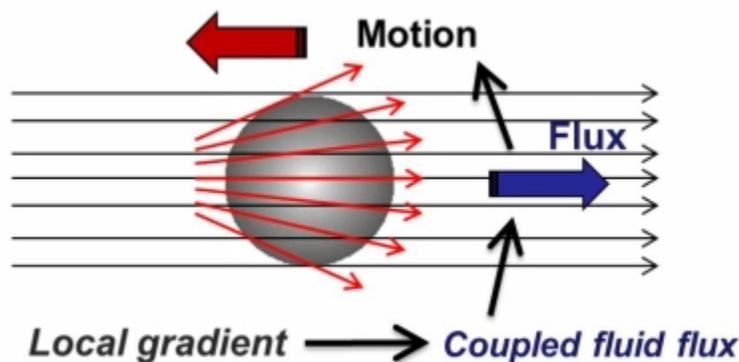
Unlike atoms and molecules, the number and symmetry of structures that self assemble from colloidal particles is restricted by the absence of directional specific bonds. Colloidal structures like the diamond lattice have been difficult or impossible to make. Here we demonstrate a general method for creating the colloidal analogs of atoms with valence: colloidal particles with chemically functionalized patches that can form highly specific directional bonds. The valences of these new “colloidal atoms” possess all the common symmetries characteristic of hybridized atomic orbitals, including sp, sp², sp³ and more. The chemical functionality of the patches is programmable and specific using DNA with single-stranded sticky ends, thereby creating colloidal atoms from which different kinds of “colloidal molecules” can be assembled. This methodology opens up the possibility of building new low-coordinated open structures, both amorphous and crystalline, which is emerging as a key design feature for assembling colloids with photonic band gaps.

COLL 48

Principles and engineering of steerable, programmed and cargo-carrying self-propelling particles

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The fabrication of complex self-propelling particles is an emerging and fascinating topic, yet few concrete applications exist to date. We will report the progress in addressing the challenges of designing complex programmable particles, and identifying areas of their practical use. First we will discuss how external uniform AC electrical fields can be used as means of providing energy, propelling and controlling the motion of miniature semiconductor diodes. These particles move by particle-localized AC and DC electrohydrodynamic propulsion and could be steered by controlling the symmetry of the AC field. In the second part of the talk we will present a new class of gel-based self-propelling particles moving by Marangoni effect in a programmed oscillatory mode. These gel boats floating on the water surface are driven by a hydrogel reservoir releasing an ethanol flux that is periodically disrupted by the bulk flows around the particles. The pulse interval and the distance propelled in a pulse by these gel floaters were interpreted based on the rate of ethanol mass-transfer. This allowed us to design particles that "dance" in repeatable periodic sequences of forward/backward, or rotary steps, and travel in complex pre-programmed trajectories on the liquid surface. We will also present new types of self-propelling floaters driven by surfactant release that have been functionalized for applications such as mixers and cargo microcarriers, and may serve as a new platform for environmental remediation.



COLL 49

Equilibrium and Non-Equilibrium Self-Assembly of Nanostructured Materials

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Self-assembly of nanoscopic components into higher-order architectures defines the forefront of fundamental nanoscience research and is important for the development of new materials with potential applications in optoelectronics, high-density data storage, catalysis, and biological sensing. In my talk, I will discuss how the peculiar nature of electrostatic, photoinduced dipole-dipole, and other forces acting between nanoscale components can mediate their self-assembly into various superstructures and materials. I will show how the interactions underlying self-assembly can be studied and understood in quantitative detail, and how they can be tailored to synthesize unusual higher-order architectures: ionic-like crystals of nanoparticles, crystalline aggregates that can be assembled and disassembled by light, as well as extremely durable and yet very flexible metallic structures. Since these materials display a range of novel optical, electrical and mechanical properties, the discussion of experimental results will be accompanied by theoretical analyses combining elements of thermodynamics, statistical mechanics, electrodynamics and elasticity.

COLL 50

Laser Triggered Release from Gold Nanorods: Using the Protein Corona

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Gold nanorods have been of great interest for therapeutic and biological applications due to their unique optical properties. In particular, the ability to heat them externally using laser excitation at the surface plasmon resonance (SPR), which can heat the

particles to high temperatures and trigger the release of a payload on the nanorod surface. However, one obstacle for practical use of nanorods both in vitro and in vivo is that as soon as they are introduced to a biological fluid, proteins and other species that are present at high concentration adsorb to their surfaces, forming a “protein corona.” This corona is impossible to prevent and can block the surface of the nanorod, as well as cause undesired side effects in targeting and biodistribution. Despite this, the protein corona has desirable and unique properties that can enhance triggered release. We form protein coronas around gold nanorods such that they can hold large quantities of small molecules and DNA. The nanorods can be excited by laser irradiation on their SPR, which heats the nanorods and disrupts the corona, releasing the drug or DNA. We are using triggered release of species from the gold nanorods for a variety of biological and therapeutic applications.

COLL 51

Photoresponsive Vesicles and Vesicle Gels

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Vesicles are nanoscale containers formed by the self-assembly of lipids or surfactants. They find application in the controlled release of cosmetics, drugs, and proteins. Researchers have been looking to create vesicles that can be disrupted by external stimuli such as light since this would allow for triggered release of encapsulated molecules with accurate spatial resolution. However, currently, most photoresponsive vesicle systems rely on the chemical synthesis of light-responsive amphiphilic molecules. In this study, we report a class of photoresponsive vesicles composed of inexpensive and commercially available cationic and anionic surfactants. These surfactants form vesicles due to ionic interactions between the cationic and anionic headgroups. When irradiated by UV light, the cationic surfactant loses its charge and, in turn, the vesicles are converted into micelles due to the loss of ionic interactions. In addition, a mixture of these photoresponsive vesicles and a hydrophobically modified polymer gives a photoresponsive vesicle-gel that can undergo a gel-to-sol transition with UV light. The vesicle gel is formed by physical coupling of hydrophobes on the polymer chains to the bilayers of vesicles. Upon UV irradiation, a vesicle-to-micelle transition occurs, thus eliminating the physical coupling and causing a gel-to-sol transition.

COLL 52

Differences in adsorption between enantiopure and racemic mixtures of chiral compounds on platinum surfaces

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Two examples are provided of chiral molecules where the racemic mixtures display different adsorption behavior than the individual enantiopure components. In the first, in-situ infrared absorption spectroscopy data are provided to show the differences in 1-(1-naphthyl)ethylamine (NEA) uptake onto platinum polycrystalline surfaces from solution. When using racemic mixtures, new features are observed, presumably associated with the 1:1 H-bonded pairing of (S)-NEA with (R)-NEA. The second example refers to the uptake of propylene oxide (PO) on Pt(111) under vacuum. In this case, the lower saturation coverages seen with the racemic mixtures, as measured by TPD and molecular beam experiments, have been explained by kinetic effects. No long-range order or evidence of individual molecular pairing was seen by STM.

COLL 53

Enantioselective adsorption and separations on chiral Au nanoparticles

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Nanoparticles can be prepared with chiral ligands that render their surfaces chiral. Au nanoparticles modified with D- or L-cysteine have been shown to adsorb chiral molecules such as propylene oxide, 2-butanol and glucose enantioselectively. Enantioselective adsorption can be detected by monitoring the rotation of polarized light during addition of a racemic mixture of chiral molecules to a solution of enantiomerically pure Au nanoparticles. Rotation of light during addition of the racemic mixture to solution occurs as a result of two phenomena: enantioselective adsorption of one enantiomer in preference over the other, and modification of its specific optical rotation by adsorption onto the Au nanoparticle. A simple model allows quantitative determination of the ratio of the enantiospecific adsorption equilibrium constants (K_D/K_L) and hence, determination of the enantiospecific difference in the free energies of adsorption ($\Delta\Delta G_{DL}$) of the two enantiomers.

COLL 54

Contributions of dispersion forces to adsorption of chiral molecules on Cu surfaces

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Bulk crystal planes with nonzero and unequal Miller indices are intrinsically chiral and possess enantiospecific properties. Using PBE-D2 dispersion corrected density functional theory (DFT), we examined the structures of dense glycine and alanine on the Cu(3,1,17)^S. The results suggest that racemic alanine can coexist with the S,S-alanine domain but not the R,R-alanine domain. Our calculations give insight into the contribution of dispersion forces in these adlayers, which had previously been examined using Non-hybrid DFT functional (Rankin, R.; Sholl, D. *Langmuir* **2006**, 22, 8096).

Non-hybrid DFT functionals cannot account for dispersion interactions in the adsorption of R-3Methycyclohexanone (R-3MCHO) on Cu surfaces. We examined this system with vdW-DF and D2 dispersion corrected DFT methods, finding that these methods overbind the R-3MCHO on Cu surfaces. The results from R-3MCHO on Cu(100) and Cu(110) indicated a possible Cu(110) reconstruction. The implications on interpreting desorption studies of 3MCHO from vicinal Cu surfaces will be discussed.

COLL 55

Enantioselective separation on a naturally chiral surface: Aspartic Acid on Cu(3,1,17)^{R&S}

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Exposure of the Cu(3,1,17)^{R&S} surfaces to gas phase mixtures of D- and L-aspartic acid lead to enantioselective adsorption and separations. A method has been developed using *L-aspartic acid-1,4-¹³C₂ and D-aspartic acid that allows mass spectrometry to distinguish *L- from D-aspartic acid. Both are exposed to the Cu(3,1,17)^R surface simultaneously to allow the adsorbed phase composition to come into equilibrium with the gas phase composition at T = 460 K. The relative coverages of *L- and D- are then determined by heating the surface to decompose the adsorbed species and determine their relative coverages by detection of ¹³CO₂ and CO₂ desorption, respectively. Quantitative determination of the relative coverages yields values of the ratios of the equilibrium constants, which show true diastereomerism, $K_R^D/K_R^{*L} = K_S^{*L}/K_S^D = 2.2 \pm 0.2$. From these, the enantiospecific free energy difference for adsorption is determined to be $\Delta\Delta G = 3.0 \pm 0.3$ kJ/mole.

COLL 56

Left Foot, Right Foot, Other Foot: Glycine and Alanine on Cu{311}

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The adsorption of amino acids on copper single-crystals has become a classic prototype for studies of surface chirality. In particular, the Cu{110} surface has attracted

much attention, with molecules such as glycine and alanine adopting a common three-point binding geometry that defines a distinct chiral "footprint". The interplay between this chiral footprint and the intrinsic chirality of the adsorbate dictates aspects of the local interaction between adjacent molecules, and this in turn influences the long-range chirality of the hydrogen-bonded networks formed when large numbers of these molecules coalesce. In this LEED, RAIRS, STM and DFT study, however, we have turned to the Cu{311} surface, which bears substantial structural similarity to the Cu{110} surface but which binds glycine and alanine in achiral three-point footprints. By "switching off" this key element of chirality, we gain insight into those aspects of long-range chirality that are directly driven by intrinsic molecular chirality rather than via footprint chirality.

COLL 57

The Effect of Tuning the Surface Chemistry and Intermolecular Amino Acid Interaction upon the Enantiospecificity on Chiral Cu Surfaces

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Intrinsically chiral structures, which can potentially be used to separate chiral molecules, can be defined by highly stepped metal surfaces. The decoration of steps on these surfaces with additional metal atoms may be one potential avenue for improving the enantiospecificity of those surfaces. The enantiospecific chemisorption of amino acids adsorbed on the pure, Pd-decorated, and Au-decorated Cu(643)^S surfaces has been examined using density functional theory (DFT) calculations. Negligible differences in adsorption energies for the most stable minima of enantiomers of alanine were found on these surfaces. There are, however, measureable energy differences between the two enantiomers of both serine and cysteine in their most stable states for all surfaces. For serine and cysteine in μ_3 adsorption geometries, no enhancement in enantiospecificity upon the step decoration is observed, while for those in μ_4 geometries, it is improved, especially on Au-decorated surface. In order to probe the contribution of intermolecular hydrogen bonding and adsorption site interaction to enantiospecificity, this study has also been extended to examine the enantiospecific adsorption of amino acids on step decorated Cu(421)^S which has a smaller unit cell than Cu(643)^S. These results provide initial information on the effect of tuning the surface chemistry and intermolecular amino acid interaction upon the enantiospecificity on intrinsically chiral surfaces.

COLL 58

Triple combination nanochemoprevention of breast cancer

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A total of 1,638,910 new cancer cases and 577,190 deaths from cancer are projected to occur in the US in 2012. There is a dire need for better strategies to prevent, diagnose and treat cancer. Widespread use of chemopreventive agents has been hampered by real and perceived toxicities associated with these agents, which are small molecules with poor bioavailability. Nanochemoprevention, which involves use of nanoparticles for delivery of chemopreventive agents has shown some promise for cancer prevention by improving the bioavailability and reducing toxicity associated with these drugs. We have developed theranostic nanometer-sized constructs that encapsulate multiple promising chemopreventive agents together with a fluorescent dye for tracking drug delivery. Nanoconstruct synthesis and drug encapsulation were characterized, and the effects of chemopreventive nanoconstructs in both monolayer and 3D cell cultures were studied. Preclinical results of a triple combination nanochemoprevention approach against breast cancer will be presented.

COLL 59

Targeted Nanoparticles for Non-Invasive Hyperthermia in Malignant Disease

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Non-invasive radiofrequency (RF) field-induced targeted hyperthermia using nanoparticles is a departure from conventional cancer treatment modalities. We have delivered metallic nanoparticles targeted to cancer cells, then exposed the cells to a non-invasive radiofrequency field to produce thermal injury. Both carbon (C60) and gold nanoparticles are not toxic *in vitro* or *in vivo* to cancer cells or normal tissues. However, cancer cells treated with these nanoparticles and then exposed to a non-invasive radiofrequency field demonstrate thermal dose-related cytotoxicity. Radiofrequency field treatment of animals treated with the targeted nanoparticles leads to significant antitumor response in hepatocellular cancer models. More complex conjugations are now being performed to include very low doses of cytotoxic agents onto the surface of nanoparticles. As a result of the cancer cell specific targeting, there is no chemotherapy-related toxicity, but there is significant synergistic enhancement of cytotoxicity combining RF-induced hyperthermia with the cytotoxic agent.

COLL 60

Beyond chemotherapy: Building a cancer nanotherapeutic exploiting tumor immunopathophysiology

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Immunotherapy-based approaches for cancer treatment are of increasing clinical interest. Principles of drug delivery and the emerging field of material design for

immunomodulation might hold significant promise for novel approaches in cancer immunotherapy since biomaterials engineering strategies enable controlled delivery of immune modulatory drugs and molecules to tissues and cells of the immune system. One tissue of significant clinical interest in a cancer setting is the tumor-draining lymph node (TDLN), which participates in cancer progression by enabling both metastatic dissemination as well as tumor-induced immune escape. Hence, the TDLN represents a novel target for drug delivery schemes for cancer immunotherapy. The influence of the immune microenvironment within TDLNs on tumor progression as well opportunities for material design to reverse this effect will be discussed. In particular, our efforts in targeted delivery of adjuvants to the TDLN via nanoparticles, which promotes antitumor immunity and hinders tumor growth, will be described.

COLL 61

Spatially defined microenvironments to study tumor angiogenesis

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The extracellular matrix (ECM) of the tumor niche provides support to residing and migrating vascular cells and presents instructive cues that influence angiogenesis. To recapitulate aspects of the tumor microenvironment, we developed both 2-D and 3-D *in vitro* systems of spatially defined ECM proteins to study vascular and cancer cell.

We first developed fibronectin-patterned surfaces to guide the ordered adhesion, growth, elongation and subsequent tubular formation of endothelial progenitor cells (EPCs). Second, we investigated the role of topography and elasticity on EC behavior using micropillared substrates. We demonstrated a combinatorial effect of topography and stiffness on EC behavior. Next, utilizing carbodiimide chemistry we were able to control the discrete molecular presentation of hyaluronic acid (HA). This allowed us to investigate the interactions of both breast and colon cancer cells with HA via high-resolution analysis of adhesion, growth and migration on HA regions. Finally, we developed spatially defined 2-D and 3-D ECM-based microenvironments to analyze the multifaceted interactions between endothelial and cancer cells *in vitro*.

These novel, miniaturized systems allow the analysis of the spatial and temporal mechanisms regulating tumor angiogenesis, and can be applied to mimic other settings to address the complex interactions taking place between various cell types in their particular environment.

COLL 62

TAL effector hybrids for modular DNA-binding and transcription control

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The ability to conditionally rewire pathways in human cells holds great therapeutic potential. Transcription activator-like effectors (TALEs) are a class of naturally occurring specific DNA binding proteins that can be used to introduce targeted genome modifications or control gene expression. We will present TALE hybrids engineered to respond to endogenous signals and capable of controlling transgenes by applying a predetermined and tunable action at the single-cell level.

COLL 63

New Materials to Investigate Abberent Mechanics in Living Cells

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This talk will describe the development of novel force-sensing surfaces (both colloidal and planar surfaces) to image integrin tension in living cells. The goal of this work is to better understand chemo-mechanical couplings at the cell surface by developing new methods to visualize force transmission in real time. All force gauges require two parts: a spring with a known force constant, and an accurate ruler. Likewise, our sensor surfaces take advantage of fluorescence resonance energy transfer (FRET) between fluorophores as a molecular "ruler" and flexible polymer chain as a reversible entropic spring with a known spring constant. The sensor allows one to quantify molecular forces with high spatial and temporal resolution for a wide range of membrane receptors and cell types. I will demonstrate the first molecular tension maps of integrin tension (which range from ~1-10 pN) during the process of focal adhesion formation.

COLL 64

Cellular Fate in 3D Elastin-Like Scaffolds is Regulated by Stiffness and Integrin Ligand Density

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We utilize recombinant protein engineering to synthesize block-copeptide scaffolds that combine elements derived from the native proteins elastin and fibronectin. Dictating the specific amino acid sequences of these designed block-copeptides affords us molecular-level control to independently tailor the biochemical and biomechanical properties of the resulting scaffolds. Given their cytocompatibility and bioactivity, these materials are ideal candidates for use as cell and drug delivery vehicles, implant coatings, and biomaterials for reconstructive surgeries. Through a series of systematic, three-dimensional (3D) culture studies, we are beginning to elucidate the optimal biochemical and biomechanical scaffold properties for two different tissue systems: (1) embryonic stem cell-derived cardiomyocytes and (2) multi-cellular neural tissue. These experiments demonstrate that both scaffold stiffness and integrin ligand density are critical material properties that can instruct cellular behavior in 3D cultures.

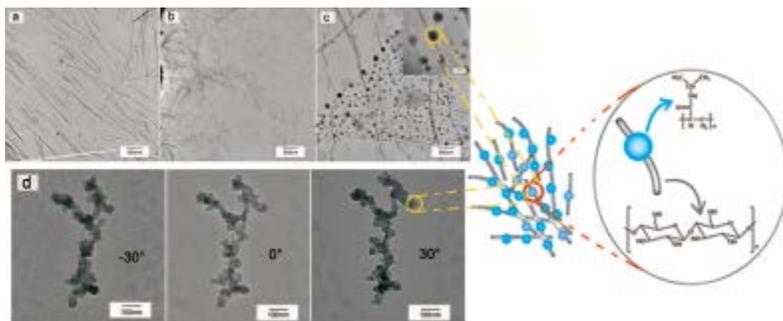
COLL 65

Intelligent responsive nano-cellulose whisker Nanogel for Interventional Therapy of Hepatocellular Carcinoma

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This paper reports the synthesis and characterization of intelligent responsive materials containing thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) polymer chains, prepared by polymerizing the grafted side chain from the BC whiskers by ATRP. The morphology of the materials was characterized by transmission electron microscope (TEM). Dynamic light scattering (DLS) was used to study the thermoresponsive properties of the grafter materials.

The polymer nanogel play the role of the interventional therapy for hepatocellular carcinoma, the in vitro cytotoxicity evaluation—CCK-8 and flow cytometric analysis were shown in paper.



TEM images shows a) the unmodified BC whisker with temperature of 25°C, b) the BC whisker-g-PNIPAM with the temperature of 25°C, c, d) the BC whisker-g-PNIPAM with the temperature of 60°C.

COLL 66

Biomimetic Self-templating Assembly and Applications

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In nature, helical macromolecules such as collagen, chitin and cellulose are critical to the morphogenesis and functionality of various hierarchically structured materials. During morphogenesis, these chiral macromolecules are secreted and undergo self-templating assembly, a process whereby multiple kinetic factors influence the assembly

of the incoming building blocks to produce non-equilibrium structures. A single macromolecule can form diverse functional structures when self-templated under different conditions. Collagen type I, for instance, forms transparent corneal tissues from orthogonally aligned nematic fibres, distinctively coloured skin tissues from cholesteric phase fibre bundles, and mineralized tissues from hierarchically organized fibres. Nature's self-templated materials surpass the functional and structural complexity achievable by current top-down and bottom-up fabrication methods. However, self-templating has not been thoroughly explored for engineering synthetic materials.

In my presentation, I will demonstrate a facile biomimetic process to create functional nanomaterials utilizing chiral colloidal particles (M13 phage). A single-step process produces long-range-ordered, supramolecular films showing multiple levels of hierarchical organization and helical twist. Using the self-templating materials assembly processes, we have created various biomimetic supramolecular structures. The resulting materials show distinctive optical and photonic properties, functioning as chiral reflector/filters and structural colour matrices. Through the genetic engineering of the M13 phages, I will also show how resulting materials can be utilized as functional nanomaterials for biomedical, biosensor and bioenergy applications.

COLL 67

Synergy between hydroxyapatite and poly(ethylene glycol) directs the physical and cell-instructive properties of a biodegradable amphiphilic tissue scaffold

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Resorbable electrospun polymer/hydroxyapatite (HA) composite materials combine scaffold biodegradability with osteoconductivity and are attractive for skeletal tissue engineering applications. However, most biodegradable synthetic polymers are hydrophobic and do not blend well with the hydrophilic HA with adequate interfacial adhesion, resulting in poor handling properties and inconsistent biological performance of the composites. We report the development of biodegradable electrospun composite scaffolds composed of an amphiphilic poly(D,L-lactic acid)-poly(ethylene glycol)-poly(D,L-lactic acid) triblock copolymer (PELA) and varying contents of HA. The synergistic impacts of the hydrophilic poly(ethylene glycol) block and the osteoconductive HA on the scaffolds' structural and mechanical properties and *in vitro* interactions with rat bone marrow stromal cells (rMSCs) are studied. Favorable interactions between poly(ethylene glycol) and HA result in a stable PELA-HA mixture that is readily electrospun into composite scaffolds with uniform fiber dimensions. The resulting scaffolds are mechanically reinforced by HA, and exhibit superhydrophilicity ($\sim 0^\circ$ water contact angle) and striking storage modulus enhancements upon hydration, likely driven by hydration-induced crystallization of the PEG blocks. These properties are in stark contrast to the inhomogeneity, inferior mechanical properties and aqueous instability exhibited by electrospun poly(lactic acid)-HA composites. The addition of HA

also improves the attachment of rMSCs to PELA and promotes spontaneous early osteochondral lineage commitment while suppressing the expression of adipogenic markers. Our findings underscore the importance of strategic integration of structural building blocks in the design of composite biomaterials that achieve enhanced performance for tissue-engineering applications.

COLL 68

Phage-enabled cell-targeting, drug and gene delivery and tissue engineering

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Filamentous phage is a biological nanofiber, a bacteria-specific virus, and also a supramacromolecule. Its surface is made of coat proteins that can be genetically modified to display foreign peptides. This talk will cover three major topics on the use of phage for developing nanomedicines and biomaterials. I will first introduce the identification of peptides that can selectively target cancer cells, stem cells or tumor tissue from a phage-displayed random peptide library. I will then describe the use of the targeting peptides to develop novel nanoparticles for targeted drug delivery to cancer cells as well as enhanced gene delivery to stem cells. Finally, I will highlight the use of genetically engineered phage for directing stem cell differentiation and tissue regeneration.

COLL 69

Mimic a blood vessel using stress-induced rolling membrane

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We describe a new strategy to fabricate tubular structures with multiple types of cells as different layers of the tubular walls. We pattern different types of cells on a 2D stress-induced rolling membrane (SIRM). When we release the SIRM to roll up into a 3D tube, different kinds of cells will be delivered into different places. These 3D tubes could mimic blood vessels in which different types of cells constitute different layers of the tubular wall. We control the cell orientation inside the tube, which can mimic their natural arrangement of the medium-sized vein in vivo. We utilize soft lithography technology to fabricate pillars on the surface of SIRM, which can ensure most cells in the tubes live for at least three days. Our method is simple and easy to access. We believe that this method will be generally useful for 3D cell culturing and tissue engineering of blood vessel.

COLL 70

Tailored matrices to explore the influence of mechanics and adhesion ligand composition on pro-angiogenic signaling from mesenchymal stem cells

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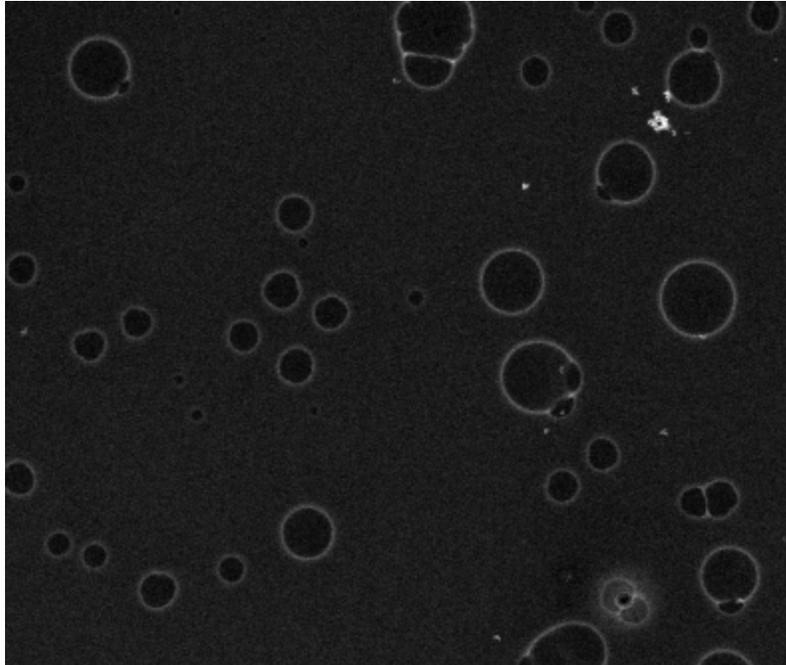
Mesenchymal stem cells (MSCs) are an exciting cell-based therapy for treating cardiovascular disease through secretion of trophic factors that promote angiogenesis. Significant strides have been made in deciphering the molecules in the MSC secretome involved in repair; however, the physical and biochemical cues in the MSC microenvironment that direct paracrine signaling are not understood. Here we present our work exploring the properties of the extracellular matrix that direct pro-angiogenic signaling from adherent MSCs. Polyacrylamide hydrogels were fabricated across a range of physiological relevant mechanical properties and functionalized with fibronectin, collagen and laminin proteins. Conditioned media from these cultures was applied to 3D matrigel matrices seeded with human microvascular endothelial cells (HMVECs). The degree of tubulogenesis was quantitated across these different combinations of ligand and stiffness. We find that the media from MSCs cultured on fibronectin conjugated 40 kPa gels promotes the highest HMVEC tubulogenesis, comparable to an endothelial growth media cocktail. In contrast, softer gels and rigid glass substrates show negligible tubulogenesis. This demonstrates the potential for an optimum microenvironment of matrix mechanics and composition to regulate pro-angiogenic signaling from MSCs. Understanding the materials cues that direct MSC secretion—and implementing these criteria into the design of biomaterials—will be critical for the development of efficacious cell-based therapeutic strategies.

COLL 71

Branched Amphipathic Peptides that Self-Assemble into Ordered Bilayer Vesicles

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Here, we describe a set of 15 & 23-residue branched, amphipathic peptides that mimic phosphoglycerides in architecture. They self-assemble and form bilayer delineated solvent-filled spheres with 50-200 nm diameters.



Whereas weak hydrophobic forces drive and sustain lipid bilayer assemblies, these structures are further stabilized by β -sheet hydrogen bonds. A linear peptide lacking the branch point shows no self-assembly. Besides encapsulating and delivering intracellularly different fluorescent dyes, we stably transformed epithelial cells with an EGF containing plasmid (EGFP-N3, 4.7kb).

COLL 72

Computational studies of antimicrobial peptides

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Antimicrobial peptides (AMPs) are thought to kill bacteria by permeabilizing their lipid membranes. We recently used implicit membrane modeling to show that four AMPs bind more strongly to membrane pores than to the flat membrane, consistent with the idea that they stabilize them. In some cases the stronger binding to pores seems to arise from the imperfect amphipathicity of these peptides. One peptide exhibiting striking imperfect amphipathicity is protegrin. We have found that protegrin requires the positive curvature of toroidal pores to bind to neutral membranes. Models of protegrin oligomeric beta barrels have been constructed and evaluated energetically. The NCNC parallel topology was found to be most stable, in apparent disagreement with solid state NMR data. We have extended this approach to pores in anionic membranes and used it to obtain insights into the lipid selectivity of AMPs. Ideas emerging from these continuum studies are tested with explicit membrane simulations.

COLL 73

Sequence determinants of spontaneous membrane-translocating peptides

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Cell penetrating peptides (CPPs) have been shown to facilitate the delivery of a wide collection of biologically active molecules and compounds into living cells and thus may have promising applications in the development of novel therapeutics. Yet the lack of tools for engineering and designing such peptides has long been a major road block in the discovery pipeline. In addition, recent studies have indicated that the cellular uptake of most currently known CPPs rely on one or more types of energy-dependent endocytotic pathways, which significantly limits their applications. Therefore, this work presented here was initiated to engineer spontaneous membrane translocating peptides (SMTPs) that move across lipid bilayers and cellular membranes in an energy-independent manner. In our lab, a previous orthogonal screen of a synthetic peptide library (N=10,368) for SMTPs revealed a conserved 9-residue motif (PLI[L/Y]LRLLR) in a family of 12-residue SMTPs that translocate rapidly without causing any bilayer destabilization. In this work, one of these SMTPs, PLIYLRLLRGQF, was selected as the template for rational iterative derivatives designed to explore the sequence determinants of spontaneous translocation. We measured the capability of translocation of these analogs in large unilamellar vesicles (LUVs) containing entrapped protease using HPLC, and we also measured vesicle permeabilization. Our results shed light on the determinants of spontaneous translocation, which may allow for the discovery and engineering of potent SMTPs to overcome the membrane barrier for drugs delivery.

COLL 74

Effects governing the activity and selectivity of membrane-permeabilizing lipopeptides

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Membrane-active peptides are often classified to act either specifically or unspecifically. The binding to a component of the target membrane or the formation oligomeric channels are, for example, considered specific effects. Unspecific action may refer to the induction of curvature stress within and between the lipid leaflet(s). The term “detergent like action” is sometimes used to describe mixed micelle formation although detergents typically permeabilize membranes by forming toroidal pores or membrane defects at concentrations well below those required for micellization.

Here we discuss a scenario that is intermediate between these classical, extreme cases and explains selectivity and high activity of, for example, lipopeptide biosurfactants. It results from the fact that principally unspecific membrane perturbation can be boosted if the perturbant is not diluted homogeneously over the membrane but sequestered into domains at high local concentration. While the destabilizing effect as such is unspecific, the interactions triggering segregation can result from specific immiscibility with certain membrane components (e.g., cholesterol). Cofactors that enhance or enhance or diminish membrane heterogeneity may enhance or inhibit the activity of such 'unspecific' membrane perturbants.

COLL 75

Structural location determines the functional roles of cationic amino acids of antimicrobial peptides

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We have been focusing on the structure-activity relationship studies of human cathelicidin LL-37. Three-dimensional structures of human LL-37 and its important fragments have been elucidated by NMR spectroscopy. These high-quality 3D structures set the stage for us to investigate the functional roles of cationic amino acids using the major antimicrobial peptide region of LL-37 as a model. It appears that Arg23 and Lys25 play an important role in modulating antimicrobial activity and membrane permeation, while Lys18, Arg19 and Arg29 tend to be more important in clustering anionic lipids as well as hemolysis. Our solution NMR study of the peptide in the presence of dioctanoyl phosphatidylglycerol yields the first piece of evidence that Arg23 is in direct contact with membranes. Taken together with 3D structures, we propose that those interfacial cationic side chains that are in direct contact with bacterial membranes are critical for antibacterial activity against especially Gram-negative bacteria.

COLL 76

A pinch of salt makes all the difference: In-situ molecular spectroscopy of chemistry at air-ice interfaces

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The air-ice interface of frozen water (snow, sea ice, etc.) is a region where important atmospheric processes are believed to occur. This nanometer to micron thick zone has physico-chemical properties which are unique to the interface and depend on (among other things) temperature and the presence of impurities. Using glancing-angle laser

Raman and fluorescence spectroscopies, we have followed the exclusion of dissolved salts and organic species to the interface during freezing and the deposition of atmospheric acids to the air-ice interface. These processes depend quite sensitively on the nature of the frozen water (salty vs. fresh) but not so strongly on temperature. I will present several recent results and attempt to relate these laboratory measurements to real environmental ice surfaces.

COLL 77

Thin Surface Films of Water on Hydrophilic & Hydrophobic Substrates: Changes in Film Behaviour and H-bonding Character Studied by Optical Spectroscopies

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Solvent molecules at interfaces often display distinct structure and bonding interactions when compared to the surrounding bulk phases. A ubiquitous example of this is found in the aqueous layers adsorbed on atmospheric particles and other environmental surfaces. In this study, we present the structure of thin, interfacial films of water (D₂O) on well-defined substrates with surface chemistries systematically varying from hydrophobic (alkanethiols with -CH₃ terminal groups) to hydrophilic (alkanethiols with -OH terminal groups) to create surfaces with water contact angles from ranging from ca. 110° > θ > 30°. Films are created by condensation or dynamic dewetting. Thicknesses trend with hydrophobicity and range from 0 to ca. 3 nm thick. These are probed by ellipsometry and PM-IRRAS, and compared with quantitative calculations for thickness and vibrational spectra of isotropic films. Unique interfacial water environments are identified in the spectral results.

COLL 78

The structure of formic acid in the liquid phase at the vapor/liquid interface

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The electronic structures of formic acid (HCOOH) and formate (HCOO⁻) have been determined in aqueous solutions over a pH range of 1.88–8.87 using XPS, PEY XAS, and DFT. The carbon 1s XPS measurements reveal a binding energy shift of -1.3 eV for deprotonated HCOO⁻ compared with neutral HCOOH. Such distinction between neutral HCOOH and deprotonated HCOO⁻ cannot be made based solely on the respective carbon K-edge PEY XA spectra. Independent of pH, the C1s → π* state

excitations occur at 288.0 eV and may lead to the incorrect conclusion that the energy levels of the π^* state are the same for both species. The DFT calculations are consistent with the experimental observations and show a shift to higher energy for both the occupied C1s (lower binding energy) and unoccupied π^* orbitals of deprotonated HCOO^- compared to neutral HCOOH in aqueous solutions.

COLL 79

Humidity-dependent surface structural changes of polyvinyl amine, polyvinyl alcohol, and polyvinyl chloride

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Polymer materials have become an indispensable resource for numerous applications including chemical/biological sensing, semipermeable membranes, and barrier materials. This is in part due to the polymers' dynamic chemical and physical surface properties that contribute to the utility of the material. In the work to be presented, surface-selective vibrational sum-frequency generation (VSFG) studies conducted on polyvinyl amine (PVAm), polyvinyl alcohol (PVOH), and polyvinyl chloride (PVC) indicate distinct surface molecular changes with variable humidity. The VSFG spectra show that the surface structure of these three polymers varies with relative humidity (0% to 100% RH), with most of the change occurring between 0% and 20% RH. Surface water modes were initially observed at 25% RH and shift to lower frequency with increasing humidity. By examining the water structure and the polymer conformation, a self-consistent picture is emerging of how the structures of these polymers adapt to varying RH.

COLL 80

Formation of low vapor pressure compounds in atmospheric aerosols: Mechanism of organosulfate formation

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Organosulfates have been observed in both laboratory-generated and ambient secondary organic aerosols (SOA). In some ambient samples, organosulfates have been found to be a large fraction of the overall composition. Organosulfates are most prevalent in acidic aerosols containing high concentrations of sulfate. Many of the observed organosulfates are multifunctional with alcohol or carboxylic functional groups along with the sulfate group. For example, these have been observed in SOA from isoprene and α -pinene photooxidation. Evidence for the formation of multifunctional organosulfates in isoprene and α -pinene SOA from epoxide ring-opening and alcohol esterification will be presented. In addition, laboratory data on the kinetics and products of these reactions will be discussed.

COLL 81

Electron spectroscopy studies of the composition and chemistry at the liquid/vapor interface

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We utilize synchrotron based electron spectroscopy of liquid micro jets to study the composition and chemistry of liquid/vapor interfaces. The variable photon energy and resulting variable photoelectron kinetic energy available at synchrotron based x-ray sources allows us to vary the depth into the solution that the experiment probes. We will present recent results on environmentally important aqueous solutes (acetonitrile, and nitric and sulfuric acid) in water solutions. A new liquid-jet x-ray photoelectron spectroscopy instrument installed at the LBNL Advanced Light Source will be described. This new instrument combines liquid-jet technology with an ambient pressure electron spectroscopy instrument. The new instrument has allowed us to study high volatility organic solutes such as acetonitrile at concentrations up to 0.9 mole fraction.

COLL 82

Raman Microspectroscopy and Vibrational Sum Frequency Generation Spectroscopy as Probes of the Bulk and Surface Compositions of Size-Resolved Sea Spray Aerosol Particles

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Sea spray aerosol (SSA), one of the largest fluxes of aerosol generated globally, can have large impacts on climate by influencing cloud formation. Despite their importance, climate impacts of SSA particles remain poorly understood due to the fact that the composition of these particles changes as a function of size and seawater composition. Bulk composition of individual particles (Raman microspectroscopy) and surface composition and structure of size-resolved particles (sum frequency generation (SFG)) were used to analyze SSA particles. These particles were produced through wave action using a unique ocean in a lab approach that minimizes contamination from ambient background aerosol particles. As will be discussed, these data provide new insights into bulk and surface compositions of SSA particles and represent a step forward in our understanding of this important class of atmospheric particles.

COLL 83

Vibrational spectroscopy of the surfaces of sea spray aerosol particles synthesized at the Scripps Hydraulics Laboratory wave flume

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The sensitivity limitations of most aerosol analytical methods prevent the direct interrogation of aerosol particle surfaces, yet it is at these surfaces that chemical and physical interactions occur with gas phase species. Size-selected sea spray aerosol (SSA) particles were collected from breaking waves created in a wave flume and analyzed using vibrational sum frequency generation (SFG) spectroscopy. Spectra indicate the presence of CH oscillators that are subject to broad molecular orientation distributions, particularly in the smallest particles. Additionally, spectra obtained from the flume surface microlayer and the smallest particles sampled above it show similar features, which suggests that the CH oscillators located at these particle surfaces may be in similar chemical environments to those found in the surface microlayer. These responses differ from those of larger particles. The molecular insights provided by this analysis are critical for developing a link between surface properties of SSA and their climate-related properties.

COLL 84

Identifying defects on oxide surfaces: Recent progress based on IR spectroscopy for single crystals as well as for powders

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The role of defects on oxide surfaces has always been considered crucial. Unfortunately, scanning tunneling microscopy, the experimental technique upon which the recent progress in understanding the chemical activity of e.g. oxygen vacancies on TiO₂ is largely based, cannot be applied to powders, the technologically most important form of oxide materials, in a straightforward fashion. As a result, the transfer of knowledge from well-defined reference systems to powder materials is very difficult. Consequently, the so-called Surface Science approach has been severely hampered with regard to understanding reactions on oxide surfaces.

Here, we present a novel method capable of investigating oxygen vacancies on both, surfaces of macroscopic, well-defined oxide single crystals as well as on powder particles [1]. We will demonstrate that the presence of oxygen vacancies on surfaces of rutile TiO₂ (r-TiO₂) can be directly identified by IR spectroscopy (UHV-FTIRS) using CO

as a probe molecule. We will also briefly discuss the main difficulties in recoding IR-spectra in reflection on oxide single crystals.

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COLL 85

Oxygen Vacancy-Promoted Coupling and Formation of Enolate for Acetaldehyde on CeO₂(111) Surfaces

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Enolate species are the key intermediates in several organic C-C coupling reactions including aldol condensation, which are important pathways in the conversion of biomass-derived feedstock to fuels and chemicals. We used a combination of RAIRS and DFT calculations to demonstrate that oxygen vacancies on CeO₂(111) are key to activate acetaldehyde and stabilize it in the enolate form (CH₂CHO). Acetaldehyde desorbs without reaction from the stoichiometric CeO₂(111) surface around 210 K. When the surface is partially reduced, acetaldehyde loses its carbonyl bond character at low temperatures. Annealing to 400 K leads to the desorption of some of the strongly adsorbed species as acetaldehyde and the appearance of another organic species, conclusively identified to be the enolate on the basis of the IR signatures, previous X-ray results, and DFT calculations. A reaction energy profile is constructed based on the surface intermediates on CeO_{2-x}(111), which finds good agreement with previous TPD results.

COLL 86

Unique Properties of Ceria Nanoparticles Supported on Metals: Novel Inverse Ceria/Copper catalysts for CO Oxidation and the Water-Gas Shift Reaction

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Inverse model catalysts composed of oxide nanoparticles supported on metal substrates have proven to be excellent benchmarks to test key components of novel catalytic materials in a systematic manner. These inverse models are prepared in-situ and can be studied with a cross section of surface science (STM, XPS, UPS, LEEM) and theoretical tools (DFT) while also being screened for catalytic activity in a reactor.

This talk will describe the properties of inverse catalysts composed of CeO_x nanoparticles supported on Cu(111) or Cu powder. Cu(111) is a standard for fundamental studies of catalytic reactions like CO oxidation and the water-gas shift (WGS). It was discovered that the addition of small amounts of ceria nanoparticles can activate the Cu(111) or Cu powder and achieve remarkable enhancements of catalytic activity. The supported CeO_x nanoparticles are extremely active for the dissociation of H_2O and O_2 , key steps in the WGS and CO oxidation reactions.

COLL 87

Structure and Dynamics of CO_2 on Rutile $\text{TiO}_2(110)$

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Adsorption, binding, and diffusion of CO_2 on reduced, hydroxylated, and oxidized rutile $\text{TiO}_2(110)$ - 1×1 surfaces were investigated experimentally using scanning tunneling microscopy, infrared reflection absorption spectroscopy, molecular beam scattering, and temperature programmed desorption and theoretically via dispersion corrected density functional theory and *ab initio* molecular dynamics. Following the saturation of bridging oxygen vacancies (V_{O} 's), additional CO_2 is found to adsorb on 5-coordinated Ti sites (Ti_{5c}) with the initial small fraction stabilized next to CO_2 on V_{O} sites. The Ti_{5c} -bound CO_2 is highly mobile at 50 K at coverages of up to 1/2 monolayer (ML). Theoretical studies show that the CO_2 diffusion on Ti_{5c} rows proceeds via a rotation-tumbling mechanism with extremely low barrier of 0.06 eV. At 2/3 ML, CO_2 diffusion is hindered and at 1 ML an ordered (2×2) overlayer with a zigzag arrangement of tilted CO_2 molecules develops along the Ti_{5c} rows. Out of phase arrangement of the zigzag chains is observed across the rows. An additional 0.5 ML of CO_2 can be adsorbed on O_b sites with a binding energy only slightly lower than that on Ti_{5c} sites due to quadrupole-quadrupole interactions with the Ti_{5c} -bound CO_2 molecules. On oxidized $\text{TiO}_2(110)$, a new stable CO_2 binding configuration is found on Ti_{5c} sites next to oxygen adatoms. Binding energy of this configuration is comparable to that of CO_2 on V_{O} sites.

COLL 88

Redox processes by photoinduced charge carriers at TiO_2 surface

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Bulk excitons formed upon UV irradiation are found to become self-trapped, consistent with the observation of temperature dependent Urbach tails in the absorption spectrum and a large Stokes shift in the photoluminescence band of anatase. The electron and hole polaron trapping energy is considerably larger at the surface making energetically favorable for the polarons to travel from the bulk to the surface where the trapping sites

correspond to undercoordinated Ti^{3+}_{5c} and O^{-}_{2c} surface atoms, or to isolated OH species in the case of a hydroxylated surface [1].

However, adsorbed molecular species can be better traps of photoinduced electrons and holes than surface undercoordinated ions or OH groups. In such cases a direct charge carrier transfer to the adsorbate takes place resulting in a net redox process. Here we explore the behaviour of a number of organic adsorbates as hole scavengers and of molecular oxygen as an electron one [2].

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COLL 89

Thermal and photochemical activation of oxygenates on titania: The roles of defects and adatoms

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The roles of dynamic defects and adatoms in determining the reactivity and selectivity of surface reactions important in heterogeneous catalysis will be illustrated for oxidation and reduction reactions on titania. Coupling reactions are induced by reduced Ti cations, including interstitials that migrate to the surface and induced C=O bond breaking in aldehydes on rutile $\text{TiO}_2(110)$. The reduced Ti centers also inhibit photochemical oxidation on the titania surface. On the other hand, O adatoms play a role in healing reduced sites, including interstitials and bridging oxygen vacancies, leading to oxidative processes on the surface. The thermal and photochemical behavior of water, methanol, organic acids, aldehydes, and ketones have been studied using a combination of reactivity measurements, imaging and density functional theory. Selected examples will be used to illustrate the dynamic nature of surfaces under reaction conditions.

COLL 90

Combined DFT and STM studies of structures and activities of rutile TiO_2 surfaces

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TiO₂ is one of the most important metal oxide materials and finds applications in wide range of fields such as catalysis, photocatalysis and biomaterials. It is also often used as model catalysts in the surface science studies aiming at elucidating some fundamental aspects in catalytic processes of metal oxides. Among its different polymorphs, rutile TiO₂ is the most abundant one, and has therefore attracted intense interest. In recent work, we have studied basic physico-chemical features of two major facets of rutile TiO₂, namely TiO₂(110) and (011), by performing combined theoretical DFT calculations and experimental STM measurements. We have found that for rutile TiO₂(110), the adsorption and kinetic performance of various molecules is largely determined by surface conditions, especially the hydrogenation caused by their own dissociation. For the rutile TiO₂(011) with unique reconstructed conformation, its structures can undergo further restructuring upon interaction with various molecules, which can dramatically affect its activity.

COLL 91

Mobile Ag-S Clusters on Ag Surfaces: Agents of Mass Transport

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In this talk, we describe the evidence for, and importance of, small complexes of sulfur and silver on silver surfaces in controlling mass transport of silver across the surface. Using the tools of scanning tunneling microscopy and density functional theory, we have characterized the role of Ag₃S₃ and AgS₂ on surfaces of Ag(111) and Ag(100), and we have shown how these two surfaces differ in terms of the stabilities and mobilities of these clusters. Recently, we have discovered larger chain-like clusters on Ag(111), built out of Ag₁₆S₁₃ monomers. We discuss the role of some of these clusters in destabilizing Ag nanoislands, i.e. their role in accelerating the process known as coarsening by which large islands grow at the expense of small islands. We present a model to explain our observation that coarsening is far slower on Ag(100) than on Ag(111) when the silver-sulfur complexes are present.

COLL 92

Substrate specificity of phosphatidylserine transport and binding proteins

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Two classes of proteins selectively interact with the lipid phosphatidylserine (PS). Some transmembrane transporters, or “flippases,” recognize PS in one monolayer of a membrane and transport this lipid to opposite surface, with the concomitant consumption of ATP. Other proteins interact with PS-containing membranes in an interfacial fashion and this binding transmits essential cell signals. The mechanisms by which these two classes of proteins interact with PS are distinct. Of the two chiral centers in PS, the PS flippase transports only the 1,2-sn-glycerol isomer of this lipid, while interfacial PS binding proteins, such as protein kinase C or clotting factors V and X, recognize selectively the L-serine stereoisomer. Modifications to other structural elements of PS result in reduction of binding to both classes of these proteins. These data indicate that two distinct binding site structures have evolved in proteins for the selective recognition of PS in biological membranes.

COLL 93

Mechanical and anhydrobiotic stabilization of vesicular and supported membranes by glycolipids and polymers

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The most widely used method to create long-circulating vesicle carriers is membrane incorporation of lipid-anchored polyethylene glycol (PEG), which sterically blocks serum protein binding, thus preventing lipid extraction, opsonization and immunoclearance. We report herein new, synthetically accessible glycolipids and polymers that provide vesicle stability in serum as well as unprecedented anhydrobiotic and cryoprotective properties: supported lipid bilayers (SLBs) retain uniformity and fluidity after air-drying and rehydration while glycolipid-protected vesicles survive freeze-drying and rehydration without fusion and minimal contents loss. Glycopolymer and glycolipid materials were also investigated as cryoprotectants for cell culture, given the known vitrification function of sugars. We anticipate that glycosystems of this type will be useful for the stabilization of synthetic membranes for delivery and SLB bioanalytical devices.

COLL 94

Lipid pixels, vesicles, and tubules: Curvature directed assembly and metastability imposed by e-beam patterned substrates

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We pixelate coexisting L_o - L_d lipid phases by supporting them with a silica substrate containing a square lattice pattern of PMMA hemispherical features formed by electron beam lithography. The pixelation pattern is metastable and, over time, the area fraction of the L_o phase on the curvature patterned regions of the substrate decreases toward zero at room temperature. Observations and kinetic rate analysis identify two competing

mechanisms to the transition to zero L_o area fraction: diffusion limited dissolution driven by an Ostwald ripening-type process and the cooperative formation of vesicles containing L_o phase lipids. By varying the substrate pattern, we can control phase partitioning and the kinetics of these two processes (dissolution vs. vesiculation) relative to each other, resulting in distinctly different compositional sorting behaviors. In addition, localized tubulation takes place with some of these underlying patterns. More recently, we have used this system to form a pixilated pattern of proteins by attaching them to a pixilated lipid phase.

COLL 95

Elastic properties of polyunsaturated phosphatidylethanolamines influence rhodopsin function

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Phosphoethanolamines (PE) comprise about 40% of retinal and synaptosomal membranes and, within these membranes, about 50% of hydrocarbon chains in PE are the six-fold unsaturated docosahexaenoic acid (22:6_{n-3}, DHA). Membranes with a high content of polyunsaturated phosphatidylethanolamines (PE) facilitate formation of metarhodopsin-II (M_{II}), the photointermediate of bovine rhodopsin that activates the G protein transducin. We determined whether M_{II} -formation is quantitatively linked to the elastic properties of PEs. Curvature elasticity of monolayers of the polyunsaturated lipids 18:0-22:6_{n-3}PE, 18:0-22:5_{n-6}PE and the model lipid 18:1_{n-9}-18:1_{n-9}PE were investigated in the inverse hexagonal phase. All three lipids form lipid monolayers with rather low spontaneous radii of curvature of 26-28 Å. In membranes, all three PEs generate high negative curvature elastic stress that shifts the equilibrium of M_I/M_{II} photointermediates of rhodopsin towards M_{II} formation. The data show that polyunsaturated lipids are important for class A GPCR activation.

COLL 96

Engineering lipid membrane domains for selective protein affinity

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One of the main features of the cell membrane is its spatiotemporal control over domain architectures, which lead to the construct of supramolecular assemblies that perform specific functions. Engineering lipid membranes to mimic this behavior could enable the creation of novel nanoscale systems for sequestration and transport, environmental sensing, hierarchical assembly, and the development of models for understanding budding and fission/fusion events. In this presentation, our most recent efforts in the study and engineering of lipid membranes to selectively bind proteins to domains will be described. Previously, we've shown that domains functionalize with metal chelates (e.g., Cu(II)-IDA, Ni(II)-NTA) selectively bound his-tagged proteins with subsequent induction of membrane curvature localized to the domain. Recently, we've explored the use of lipid structure and multivalent binding interactions to facilitate temporal control over domain formation. Our investigations further extend into how protein complexes on lipid domains may enable the development of nanoscale transport systems.

COLL 97

Strategies for optimizing lipid-based delivery of nucleic acids to cells for gene delivery and gene silencing: Synthesis, live cell imaging, and transfection efficiency studies

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Cationic liposomes (CLs) are studied worldwide as carriers of DNA and short-interfering-RNA (siRNA) for gene delivery/silencing and related clinical trials are ongoing worldwide [see <http://www.wiley.com/legacy/wileychi/genmed/clinical/>; *Advances in Genetics, Vol. 53: Non-Viral Vectors for Gene Therapy* (2nd ed. Part I, Elsevier, London 2005)]. Enhancement of transfection efficiency and silencing efficiency by cationic liposomes requires an understanding of the nature of interactions of complexes with cell surfaces, events leading to release of complexes from endosomes, and tracking and determination of the complex fate within the cytoplasm [see K. K. Ewert et al. *Topics Curr. Chem.* **2010**; C-L Chan et al. *Biomaterials* **2012**]. Our studies employ a combination of strategies including, custom synthesis of lipids and cyclic-peptide-PEG-lipids, x-ray scattering, transfection efficiency, and live cell imaging with Rab-GFP proteins [R. Majzoub et al. to be submitted]. Results of recent studies on cell-targeting, endosomal escape, and organelle tagging (for spatial-temporal tracking of complexes) will be presented. Funded by NIH grant R01 GM59288.

COLL 98

Highly organized plasmonic structures for SERS sensing

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Surface enhanced Raman scattering (SERS) spectroscopy is a powerful ultrasensitive technique which allows detection down to single molecule levels. The production of SERS substrates is based on the generation of hot spots created by plasmonic nanoparticles. However, the controlled formation of these hot spots over large areas is still a challenge in order to produce homogeneous and reproducible SERS intensities over large areas.

We report novel methods to produce highly organized structures made of plasmonic nanoparticles in a macro-scale range using a completely lithography-free approach. Monolayers, supercrystals, and tuneable periodic linear arrays, were created via spin coating, confinement controlled drying, and their combinations.

These structures, were effectively use for sensing using SERS showing very good reproducibility among big areas. This fact, make them perfect candidates as ultrasensitive substrates for SERS due to the controlled formation of hot spots. Which provide high and uniform SERS enhancement over extended areas.

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COLL 99

Use of silver nanoparticles to conduct Surface Enhanced Hyper Raman Spectroscopy (SEHRS) of biological dye molecules

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Surface-Enhanced Hyper-Raman Spectroscopy (SEHRS) is a powerful nonlinear optical process used to probe the structure of surface-bound molecules. We utilize the enhancements from both silver nanoparticle clusters and resonance hyper-Raman

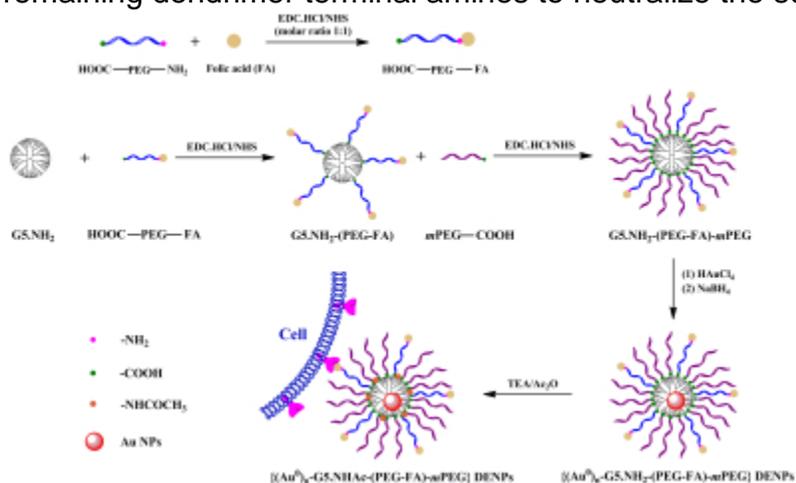
scattering to map one-photon inaccessible states in dye molecules of multi-photon interest. Our wavelength-scanned experiments are further compared to theoretical calculations, where it is found that non-Condon terms (B-term) dominate the spectra. The use of two-photon resonant states and surface enhancements provides the ability to detect molecules in very low concentrations, possibly on the single molecule level. Due to the enhancements of plasmonic nanoparticles, lower excitation powers can be employed than utilized in normal hyper Raman experiments. Our work should contribute greatly to the understanding of the rich electronic structures that direct two-photon optical processes on plasmonic metal surfaces.

COLL 100

Folic acid-modified PEGylated dendrimer-entrapped gold nanoparticles for *in vitro* and *in vivo* targeted computed tomography imaging of tumors

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We report the synthesis and characterization of folic acid (FA)-modified PEGylated dendrimer-entrapped gold nanoparticles (Au DENPs) for *in vitro* and *in vivo* targeted CT imaging of tumors. In this study, amine-terminated poly(amidoamine) dendrimers of generation 5 (G5.NH₂) modified by polyethylene glycol (*m*PEG-COOH and FA-PEG-COOH) were used as templates to entrap Au NPs, followed by acetylation of the remaining dendrimer terminal amines to neutralize the surface potential of the particles



. The formed $\{(Au^0)_{300}\text{-G5.NHAc-}m\text{PEG-(PEG-FA)}\}$ DENPs were characterized by UV-Vis spectrometry, ¹H NMR, transmission electron microscopy. MTT cell viability assay and flow cytometric analysis were used to assess the cytotoxicity of the particles. We show that the formed Au DENPs are stable, cytocompatible at the Au concentration up to 300 μM, and have much higher x-ray attenuation intensity than Omnipaque (an

iodine-based CT imaging agent) under similar concentration of the active element. Moreover, the developed Au DENPs enable effective CT imaging of KB cancer cells with high FA receptor expression *in vitro* and the KB xenograft tumor model *in vivo*. These findings suggest that the designed Au DENPs can be used as a promising contrast agent for targeted CT imaging of tumors.

COLL 101

Coupling between Exciton and Plasmon in Gold-Quantum Dot Nanoconjugates for Fluorescent Enhancement and Protein Detection

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Metal-enhanced fluorescence arises from the near-field interaction between fluorophores and metal nanostructure when a dye molecule is placed very closely to the surface of a metallic nanoparticle. The fluorescence enhancement is thought to be associated mainly with the increased radiative decay rate of the nearby fluorophores, but recent reports have suggested that strong coupling between the surface plasmon and the photon emitted by the emitter can take place when the electromagnetic field enhancement is very high. In such cases, the resonant exciton-plasmon interactions modify exciton wave functions and surface plasmon modes, leading to changes of exciton and surface plasmon resonance energies that are much larger than the cases with increased radiative decay rate alone. Here, we report a new experimental system that exhibit the strong coupling between exciton-plasmon interactions. Water-soluble CdSe/ZnS core/shell QDs were chemically bonded to popcorn-shaped gold nanoparticles (PS-AuNPs). The separation distance between QD and PS-AuNP was fixed at 6 nm. The strong exciton-plasmon coupling in our system resulted in >100 times fluorescence enhancement. Finite difference time-domain (FDTD) simulations were conducted to investigate the enhanced electric field near QD at various excitation wavelengths. A linear relationship with the measured fluorescence enhancement was achieved. As the fluorescence enhancement is highly sensitive to the local electric field environment, we attached biomolecules onto the PS-AuNP-QD and found that the presence of localized biomolecules can influence the fluorescence enhancement and can be used as a readout for biomolecule detection.

COLL 102

New synthetic methods of colloidal plasmonic nanoparticles for molecular and protein sensing

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Plasmonic nanoparticles are characterized by having the localized surface plasmon resonance (LSPR) spectrum whose frequency is sensitive to the nanoparticle shape

and the dielectric function of the surrounding molecules around its surface. For this reason they are useful in sensing. Different shapes including hollow spherical, double shell nanocages, and silver nanorods of different aspect ratios are synthesized in colloidal solutions. New technique is discussed in which to synthesize silver nanorods with different aspect ratio and based on seedless technique. In this method different rods of different aspect ratio can be prepared from the same synthetic patch. The sensing efficiency of the plasmonic nanoparticles in colloidal solutions and on the surface of a substrate is also presented. The simultaneous detection of different proteins in solution is shown to increase by using glycans which bind specifically to each protein.

COLL 103

Accepting and embracing practical "barriers" for solution-phase nanoparticle sensors

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Nanomaterials are used in many biomedical and environmental sensors. Undoubtedly, for more nanoparticle based sensors to be widely utilized, the irreproducibility of the nanosensor measurements must be acknowledged and overcome. Herein, both the electromagnetic and physical stability of gold nanomaterials will be measured and modeled as a function of surface chemistry and general solution conditions. These results will reveal that solution and storage conditions of nanoparticles can be selected strategically to promote nanomaterial stability and to increase shelf-life. Additionally, simple quality control measures can be implemented to promote reproducible plasmonic and SERS detection of small molecules. The practical importance of nanoparticle engineering, surface chemistry, and stability will be emphasized and related to nanosensor applications.

COLL 104

Individually SERS Active Nanotags with Dual Functionalities

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We have developed individually SERS-active nanotags that uniquely function both as a reporter and a sensitive platform for SERS measurements of analytes of interest. Hollow Au-Ag alloy nanoshells with a porous wall were synthesized by galvanic replacement reaction, and were subsequently loaded with thiocyanate (SCN⁻) tag molecules. The open structure of the nanoshells was filled with Ag via citrate reduction,

sealing SCN⁻ inside the core-shell nanostructure. Nanotags show a linear correlation between the SERS intensity of the encapsulated SCN⁻ and the number of nanoparticles. The SERS intensity of SCN⁻ is insensitive to environmental variants and can therefore be reliably used as an internal reference for quantitative measurements. Unique to previously documented nanotags that serve solely as a beacon, our nanoparticles with encapsulated SCN⁻ can function both as such and ultra-sensitive substrates for SERS measurements of analytes of interest.

COLL 105

Interactions between plasmonic nanoparticles and proteins investigated by correlation spectroscopy with single particle sensitivity

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We present *in situ* studies on the adsorption of proteins to plasmonic nanoparticles. We have implemented luminescence and scattering correlation spectroscopy with single particle sensitivity as an optical tool to quantify changes in the nanoparticle Brownian motion resulting from protein adsorption onto the nanoparticle surface. We are able to measure changes in the hydrodynamic radius of only a few nanometers corresponding to protein monolayer coverages. Nanoparticle aggregation can be distinguished by analyzing the collected photon trajectories for the intensity and number of individual bursts caused by single objects passing through the confocal excitation volume. We also measure adsorption isotherms to elucidate the thermodynamics of protein binding. For an accurate implementation of correlation spectroscopy methods it is furthermore necessary to understand how the collected optical signal scales with nanoparticle size and shape. We are able to obtain this information by correlated electron microscopy and single particle spectroscopy of immobilized plasmonic nanoparticles.

COLL 106

Optically calculating quantities of hybrid-1 and hybrid-2 G-quadruplexes in telomeric sequences using NSET

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Telomeres are noteworthy in anti-cancer research due to the difference in telomere preservation between healthy cells and cancerous cells. More specifically, folded G-quadruplex structures observed in telomere DNA are studied to shed light on sequence stability and folding. Despite success in identifying plausible G-quadruplex formations through molecular dynamics calculations, X-ray crystallography, and proton NMR, these methods lack the ability to obtain population distributions of various G-quadruplexes in Tel22, the native telomeric sequence. In particular, relative hybrid-1 and hybrid-2

structural populations are not known, even though mixtures of these structures are observed in K^+ solution. Here we employ Nanometal Surface Energy Transfer (NSET) between a dye-labeled Tel22 sequence and a gold nanoparticle to distinguish and quantify the multiple G-quadruplex formations of Tel22 in biologically relevant solutions. Where X-ray crystallography and proton NMR fall short in extracting population data, NSET offers cell-simulated hybrid-1 and hybrid-2 structural distributions based on distant-dependent dye lifetimes.

COLL 107

Remotely Controlled Hybrid Nanomaterials: Light, Ion, and Magnetically-controlled

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Microcapsules and Nanorods

We report on fabrication of thin shell microcapsules from amphiphilic star block copolymers and natural polyelectrolytes based upon silk fibroins with shell porosity and permeability reversibly controlled either by surrounding pH values or light-induced changes in ion balance. In another story, uniform and mobile ferromagnetic layers with open organized lattice from functionalized magnetic nanorods were assembled on functionalized coatings with their positioning and orientation readily and remotely tuned by distant magnetic field.

COLL 108

Electrochemically controlled release of molecular guests from redox responsive polymeric multilayers and devices

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A novel platform technology for a tunable molecular payload release, employing complex release profiles, from electrode surfaces is reported. Organometallic poly(ferrocenyilsilanes) (PFS), featuring redox responsive ferrocene units in their main chain, are used as a carrier medium to prepare thin films by the layer-by-layer (LbL) method for redox triggered delivery. These films form the active component of the device. The release of guest molecules from PFS multilayer templates was monitored by fluorescence spectroscopy by varying the supporting electrolyte, the ionic strength of electrolyte, redox inactive components, blocking layers and the molar mass of the polymer. Incorporation of TRITC and Alexa 488 dye molecules into PFS multilayers, at

various depths of the film, enabled tuning of the release profiles with different release kinetics for each component. Composite multilayers encompassing dual redox and pH responsive polyelectrolytes show double responsive control over the dye release. Finally a device was build featuring the combination of a microelectrode array (MEA) and PFS multilayers to demonstrate area addressable pulsed release for potential applications.

COLL 109

Remotely activated patterned polymer microcapsules and microchamber arrays

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A number of applications in bioengineering, sensing, and microanalysis requires precisely controlled microencapsulation and release. Polymer microcapsules assembled in layer-by-layer fashion have been demonstrated as a promising delivery system for different classes of compounds due to a variety of loading routines and release options, such as spontaneous sustained release, release triggered by chemical and physical-chemical stimuli, and remote physical impact. Patterning of microcapsules on a plane solid substrate introduces the site specificity of release. Capsules in a pattern can be activated as a group or even one by one by remote physical stimulus like illumination with a laser beam. This paper reports on a physical entrapping of polymer multilayer microcapsules in microwells of a pre-patterned substrate and fabrication of polymer multilayer microchamber arrays. The patterned capsules and chambers can be loaded with various actives, serve as microreactors, and be remotely ruptured by a laser beam releasing the content on demand.

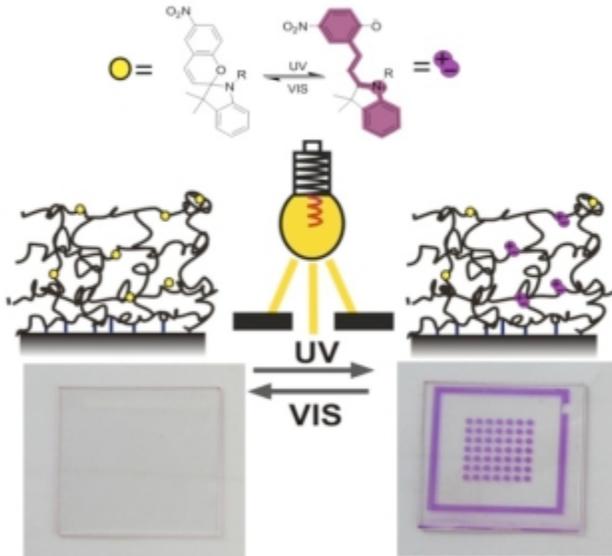
COLL 110

Stimuli-responsive polymer networks at surfaces that can be switched by light

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Smart polymers at surfaces that react to external stimuli are of great interest for the design of materials with switchable surface properties (e.g. adhesion, wetting, or absorption). While switching of stimulus-responsive polymers by temperature, pH or salt is already investigated in many scientific studies, polymers that react to other stimuli, such as for example light, are less frequently addressed, in particular, if these molecules are confined as thin polymer layers at surfaces. Here, we introduce surface-attached *Spiropyrane*-polymer hydrogels that respond to light with a dynamic and reversible change of their chemical structure. Upon irradiation with UV-light, a reversible

change within the light-sensitive Spiropyran-group occurs, which switches this function from a non-charged, hydrophobic spiropyran to a zwitterionic, hydrophilic merocyanine form. We will show that the latter is accompanied with a change in surface-properties, and thus light-switchable wetting as well as specific capture of ions by the film can be dynamically modulated.



COLL 111

Light-activated opening of gold-nanoparticle modified capsules

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Polyelectrolyte capsules are modified with Au nanoparticles in their walls. Their uptake pathway by cells will be discussed.[1] Inside cells capsules will be opened by light-mediated heating of the gold nanoparticles and the content from the capsule cavity is released. This will be used to stimulate intracellular reactions. Present state technology is discussed towards future in-vitro and in vivo applications.

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COLL 112

Layered, light-responsive polymer nanocomposites

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We report on layered soft materials which exhibit programmable, nanostructure-encoded, reversible shape changes in response to light irradiation. The use of gold nanoparticles grafted with a temperature-responsive polymer with layer-by-layer (LbL) assembly allowed placement of plasmonic structures within specific regions in the film, while exposure to light caused localized material deswelling by a photothermal mechanism. Precise localization of brush-decorated gold nanostructures within LbL films yielded materials allowing remotely controlled unidirectional changes in material swelling. We discuss the equilibrium swollen states and mechanical properties of LbL assemblies. Incorporation of dissimilar plasmonic nanostructures (solid gold nanoparticles and nanoshells) within different material strata enabled controlled shrinkage of specific regions of hydrogels at specific excitation wavelengths. The demonstrated novel ways to dynamically control nanocomposite swelling anisotropy and shape are potentially useful in optically manipulated functional devices.

COLL 113

Remote-controlled pulsed release from Layer-by-Layer engineered hydrogels beads

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Microscale pulsatile release devices hold potential in different fields of application including drug delivery, tissue engineering, active coatings, microreactor engineering, microfluidics etc... In stead of opening a diffusional barrier, which is the case for most stimuli-responsive systems, pulsatile release systems 'eject' their payload with a certain momentum that allow the ejected species to be transported at higher velocities than would be the case by mere Brownian motion. Here we design such systems by engineering degradable hydrogel beads with a Layer-by-Layer coating. Dextran was modified with polymerizable methacrylate moieties that are connected to the dextran backbone via a hydrolysable carbonate ester link. Through phase separation in aqueous medium with at concentrated PEG solution, followed by radical polymerization of the pending methacrylate moieties, crosslinked hydrogel beads are obtained. Layer-by-Layer (LbL) coating of these beads with oppositely charged polyelectrolytes and metal nanoparticles allows designing two types of systems depending on the dextran concentration in the hydrogel beads and the mechanical strength of the LbL coating. A first system at high dextran concentration yields exploding capsules by addition of alkaline medium to hydrolyze the carbonate esters. A second system a low dextran

concentration yields light-sensitive capsules that eject their payload upon laser irradiation of metal nanoparticle clusters on the capsule shell.

COLL 114

Programming the Release Properties of Microcapsules

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In this work, we present programming the release properties of biocompatible and biodegradable poly(DL-lactic-co-glycolic) acid (PLGA) microcapsules by using water-in-oil-in-water (W/O/W) double emulsions as templates. These microcapsules can encapsulate both hydrophilic and hydrophobic agents, and their release sequence can be “programmed” by changing the morphology of PLGA microcapsules and incorporating gold nanorods. The PLGA microcapsules with uniform core-shell morphology release the inner hydrophilic encapsulants upon near-infrared light irradiation, whereas snowman-like microcapsules release hydrophobic encapsulants under the same condition. We also demonstrate that the size of PLGA microcapsules can be tuned by osmotic pressure annealing. The final size of PLGA microcapsules depends on the initial size of inner droplets and the salt concentration of both the inner and the outer aqueous phases. The osmotic pressure annealing offers a straightforward method to control the size of microcapsules as well as the concentration of encapsulated species. Our findings provide critical guidelines in designing programmable microcapsules for various biomedical applications that require sequential release of agents of different polarity.

COLL 115

Preparation of ultra-thin cellulose nanofibril-based hollow capsules using Layer-by-Layer deposition

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In the field, hollow microcapsules with nanometer thin shells have been prepared by a sequential deposition of polymers and/or nanoparticles on different destructible substrates, e.g. dissolvable microparticles or at the liquid/gas interface. To make these capsules industrial interesting, reducing the number of deposition layers together with avoiding capsule collapse upon drying is a necessity. We show that this can be achieved by adsorbing the strong and renewable cellulose nanofibrils (NFC), anionically

and cationically modified, on to dissolvable particles. In addition, to increase the shell toughness, the elastic biopolymer xyloglucan (XG) is deposited between each NFC layer. This combination of NFC and XG enables production of shells after only a few deposition layers, withstanding core removal and drying.

COLL 116

Exploring Enantioselectivity on Chirally Modified Surfaces in Ultrahigh Vacuum

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The mode of operation of heterogeneous chiral modifiers can be classified into those operating as templates, where several modifier molecules act in concert to define a chiral adsorption site, or one-to-one modifiers that form a docking complex between the modifier and a prochiral reactant. Enantioselectivity is measured by adsorbing chiral probe molecules onto chirally modified surfaces. Templating is illustrated using aminoacids on Pd(111). Scanning tunneling microscopy (STM) reveals that some aminoacids form tetrameric units, and others form dimers. Only those aminoacids that form tetramers are enantioselective implying that the tetramers act as templates.

Naphthylethylamine (NEA) is proposed to act as a one-to-one modifier. The interaction between NEA and a prochiral reactant, methyl pyruvate, is explored using STM. Possible docking complexes are identified using density functional theory and the simulated images are compared with experimental images.

COLL 117

Combined Non-Covalent and Chemisorption Driven Prochiral Steering of α -Ketoesters at Sites Formed by Chiral Molecules on Pt(111)

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Stereodirection by chiral molecules adsorbed on Pt(111) was studied by observing the stereospecific binding of prochiral molecules at individual chiral sites. By combining DFT calculations and STM imaging it was possible to define both the regiochemistry and the stereochemistry of the binding interactions. We present STM measurements of the interaction of two representative prochiral molecules with two chiral molecules. A hierarchy of metal-molecule and molecule-molecule interactions are found to control the stereochemistry of modifier-substrate complexation. These include chemisorption into specific adsorption geometries, conventional H-bonding, CH \cdots OC bonding and steric repulsion. Control of the binding configurations was explored by tuning the structure of

the chiral molecule. These studies provide information and insight on heterogeneous asymmetric hydrogenation reactions on metal surfaces.

COLL 118

Asymmetric autocatalysis triggered on enantiotopic surfaces of achiral organic and inorganic crystals

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The origin of chirality of organic compounds has attracted broad attention. Achiral crystals have rarely been considered as the origin of chirality. Some achiral crystals are known to have enantiotopic faces. 2-(*t*-BuMe₂silylethynyl)pyrimidine-5-carbaldehyde is an achiral crystal with enantiotopic faces. When vapor of diisopropylzinc was reacted with enantiotopic surface of the crystal, chiral pyrimidyl alkanol with the corresponding absolute configuration of moderate enantiomeric excess was formed. The subsequent asymmetric autocatalysis with amplification of ee afforded pyrimidyl alkanol with >99.5% ee. Moreover, enantiotopic surface of naturally occurring gypsum (calcium sulfate 2H₂O) was found to act as chiral initiator of asymmetric autocatalysis. Thus, in conjunction with asymmetric autocatalysis, enantiotopic surfaces of achiral organic and inorganic crystals work as the origin of chirality.

COLL 119

Adsorption and self-assembly of tetrahydroxybenzene on Cu(111)

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The adsorption of (1,2,4,5)-tetrahydroxybenzene on Cu(111) is investigated by density functional theory calculations to complement recent experimental results obtained by Scanning Tunnelling Microscopy (STM) and X-ray Photoelectron Spectroscopy [1]. At room temperature core level spectra and contrast differences in the STM images suggest that some of the molecules have dehydrogenated to form (2,5)-dihydroxybenzoquinone. This is supported by calculations showing that the dehydrogenation reaction is energetically favourable at the experimental conditions.

Annealing of the sample leads to a complete dehydrogenation of the molecules. The resulting dihydroxybenzoquinone forms a close-packed structure and a porous metal-coordinated network which coexist on the surface. A systematic search covering orientational degrees of freedom and different configurations of adatoms is conducted to find the detailed structures of the two overlayers. A comparison reveals that the energetically preferred structure depends on the coverage of the surface.

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COLL 120

Guiding the formation of single-handed enantiomeric porphyrin domains using kinked and chiral stepped surfaces

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The self-assembly of nickel tetraphenyl porphyrin (NiTPP) on achiral Au(111), which includes randomly located kinked steps, and chiral Au(1036 1070 1035) and (1036 1035 1070) surfaces has been studied using UHV scanning tunneling microscopy. The clean surfaces of the achiral and chiral gold crystals were characterized with STM. Subsequently, NiTPP molecules were deposited on each surface. On achiral Au(111), the porphyrins assemble into racemic mixtures of enantiomerically resolved domains. It is concluded that, on large flat terraces, intermolecular interactions are the dominant factor in the chiral assembly. Moreover, it is found that the chirality of the molecular array can be guided using the handedness of locally kinked step edges. Preliminary work has begun on the chiral crystal surfaces. Initial findings suggest that the chirality of the kinked step edges induces formation of a single-handed domain of molecules across a terrace.

COLL 121

Pasteur Revisited: Chiral Separation by Crystallization on Self-Assembled Monolayers

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Chiral resolution is commonly used in the pharmaceutical industry given the large number of chiral drug candidates. Enantiomers possess identical physical and chemical properties in an achiral environment but exhibit different properties in chiral environments, such as biological systems. Therefore a pure enantiomer is preferred over the racemate in many marketed dosage forms due to the potential safety and efficacy issues. Recently chiral surfaces based on self-assembled monolayers (SAM) and Langmuir-Blodgett films have been used to study the influence of functionalized surfaces on nucleation, polymorphism, and selective orientation of crystals, as well as the selective crystallization of one enantiomer or the other. In this work we revisited Pasteur's crystallization based chiral separation and obtained >90% pure L-glutamic acid by using a D-penicillamine self-assembled monolayer as the resolving auxiliary and

manually removing enantiopure crystals identified through Raman microscopy. Identical conditions in bulk solutions yielded only racemic crystals.

COLL 122

Chiral interfaces between gold nanoclusters and thiols

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Recent experimental and theoretical breakthroughs have revealed the atomistic details of the curved inorganic-organic gold-thiol interface of thiol-stabilized gold nanoclusters, responsible for their chiroptical activity. This talk focuses on the few experimentally resolved cases by comparing Au₂₅, Au₃₈, and Au₁₀₂ clusters (1,2,3) and discusses computational predictions for Au₄₀, Au₅₅ and Au₁₄₄ clusters. (4) Future applications of these interesting novel nano-materials may be realized now once their fundamental structure - property relationship are being uncovered.

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COLL 123

Smart microgel-stabilized emulsions: Fundamental properties and applications in biocatalysis

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Soft, multi-sensitive thermo- and pH responsive microgels are able to stabilize oil-in-water emulsions, the stability of which can be controlled by pH and / or temperature. Interfacial rheology data indicate the relevance of viscoelastic properties of the interface for emulsion stabilization and it is even possible to prepare stable emulsions with oppositely charged droplets. The structure of the microgels at the oil-water interface was observed in cryogenic electron microscopy and characteristic differences as compared to rigid particles were found: The microgels are strongly deformed at the interface and protrude only little into the oil phase. The microgel layer at the oil water

interface is thus very different as compared to Pickering emulsions involving rigid particle stabilizers.

Emulsion stability can be controlled via chemical composition and morphology (e.g. core-shell architecture) of the microgels. This allows tailoring microgel properties and emulsion stability for applications. As one example, we will discuss enzyme-catalysed reactions of oil-soluble substrates.

COLL 124

Understanding the Multiple Orientations of Isolated Superellipsoidal Hematite Particles at the Oil-Water Interface

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Non-spherical particles can have the potential to adopt multiple orientations once adhered to a liquid-liquid interface. In this work we combine simulations and experiments to investigate the behaviour of an isolated microscopic hematite particle of superellipsoidal shape. We show that this microparticle can adopt one of three orientations when adhered to a hexadecane-water interface. Two of the orientations, and estimates for their relative populations, could be assigned to two thermodynamic minima on the energy landscape as generated through both free-energy minimization and particle trajectory simulations. The third orientation was found to correspond to a kinetically-trapped state, existing on certain particle trajectories in a region of a negligible gradient in free energy. To underpin the simulations the individual orientation of a set of 100 isolated particles was explored by means of scanning electron microscopy (SEM) using the gel trapping technique as a tool. Atomic force microscopy (AFM) was additionally used to support the experimental findings. This is the first example of such a kinetic metastable state being observed for particles at liquid-liquid interfaces.

for more info see: www.bonlab.info

COLL 125

Thermodynamically Stable Emulsions Stabilized by Janus Dumbbells

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Janus particles have two sides with different, often opposite, surface properties. Janus dumbbell is one type of Janus particles that consists of two partially fused spherical lobes. It is possible to independently control the geometry and surface wettability of

Janus dumbbells. Janus dumbbells can also be produced in a large quantity, making them useful for practical applications such as emulsion stabilization. In this work, we calculate the free energy of emulsion formation using amphiphilic Janus dumbbells as solid surfactants. In contrast to kinetically stable emulsions stabilized by homogeneous particles, emulsion stabilized by Janus dumbbells can be thermodynamically stable. There also exists an optimal radius of droplets that can be stabilized by infinite or limited number of amphiphilic dumbbells in the continuous phase. We demonstrate that the optimal radius of dumbbell-stabilized droplets can be predicted based on the volume of the dispersed phase and the volume fraction of dumbbells in the continuous phase. We believe our calculation will provide guidelines for using Janus dumbbells as colloid surfactants to generate stable emulsions.

COLL 126

Carbon Dioxide-in-Water Foams Stabilized with Interfacially Active Nanoparticles

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A relatively new concept for stabilizing carbon dioxide-in-water foams for enhanced oil recovery and CO₂ sequestration is to design nanoparticles that adsorb at the interface. A concept of hydrophilic/CO₂-philic balance (HCB) may be defined to describe the surface chemistry on the nanoparticles, which influences stabilization of carbon dioxide-in-water (C/W) foams. The HCB has a large effect on the stabilities and viscosities of the foams. The apparent viscosity of C/W foams with fine texture (bubble sizes less than 100µm) increased up to 120 fold of the value without nanoparticles upon foam generation by shearing CO₂ and water phases in a beadpack. Long-term stability of nanoparticle-stabilized C/W foams was also demonstrated in terms of foam resolution. The ability to achieve viscous and stable C/W foams with properly designed nanoparticles could offer an alternative to conventional surfactants.

COLL 127

Novel Pickering emulsions based on pH-responsive poly(*tert*-butylaminoethyl methacrylate) latexes

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The tendency of colloidal particles to reside at a fluid-fluid interface is the basis of the behavior of Pickering emulsions. Despite their surface activity, homogeneous colloidal particles are not amphiphilic in nature. In contrast, Janus particles with anisotropic surface wettability have the potential to be more strongly trapped at an interface if their adsorption leads to the contact of each hemisphere with its favored phase. As this preferred orientation results in restricted rotational freedom, significant increase in emulsion stability has been predicted by enhancing the particle amphiphilicity. Since these emulsions are kinetically stabilized, it is important to study the dynamics of amphiphilic particles approaching an interface in order to clarify whether amphiphilic particles have the right orientation toward the preferred phase before jumping to an interface or if this orientational adjustment happens once the particle is sitting at the interface. In spite of the vast literature on colloidal particles at interfaces, little information is available with respect to the dynamics of colloidal particles moving towards and binding to an interface. Even less is known regarding the orientation of the Janus particle during the insertion process.

We have investigated the movement of Janus colloids toward the interface between two immiscible fluids with digital holography microscopy. Through this optical technique, we determine the three dimensional position of a homogenous colloidal particle as a function of time as it moves to the interface and relaxes toward equilibrium. Implementing this tool for studying the dynamics of Janus particle adsorption to an interface requires tracking the orientation of the particle through time. By analyzing this data, we obtain the cap angle as a function of the distance from the interface. In addition, we have also explored Janus particle adsorption to a liquid-liquid interface using molecular dynamics simulations and will compare the results to the experimental observations.

COLL 130

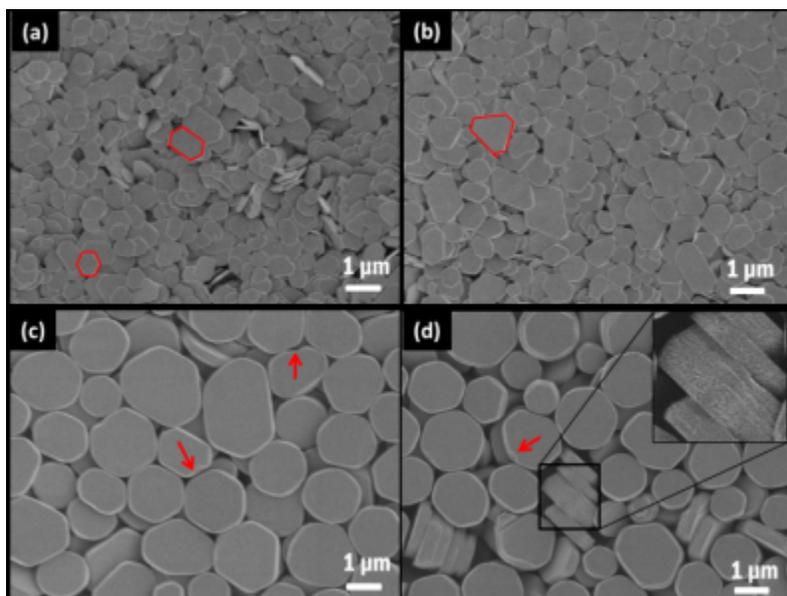
Pickering emulsions and foams stabilized by highly anisotropic nanoplates

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Platelets or disk-like nanoparticles are widely used as building blocks for nanostructures in colloidal self-assembly approach. They have found various applications in polymer nanocomposites, biomimetic materials, functional membranes, Pickering emulsions, and discotic liquid crystal studies. The shape, size, and size polydispersity of these

nanoparticles are key factors in their applications. Systematic experiments in our lab revealed that regular-shaped α -zirconium phosphate crystalline disks with a size-to-thickness ratio from 1 to 50 and size polydispersity as low as 0.2 can be obtained through hydrothermal treatment in 3 M to 15 M phosphoric acid solutions. Extremely anisotropic platelets were obtained via exfoliation of these crystals, and amphiphilic nanoplates (Janus and Gemini plates) were obtained by exfoliation following the chemical functionalization of the surfaces of the crystals. We will present the systematic study of the Pickering emulsions and foams stabilized with these nanoplates.

1. "Pickering Emulsions Stabilized by Amphiphilic Nano-Sheets" A.F. Mejia, A. Diaz, S. Pullela, Y. Chang, M.S. Mannan, A. Clearfield, and Z. Cheng, **Soft Matter**, 2012, 8, 10245-10253.
2. "Stabilization of Pickering Foams by High- aspect-ratio Nano-sheets" J. S. Guevara, A. F. Mejia, Y. Chang, M. Shuai, M.S. Mannan, and Z. Cheng, **Soft Matter**, 2012 (accepted).



SEM of α -ZrP disks synthesized in different phosphoric acid concentrations: (a) 3M, (b) 6M, (c) 12M, and (d) 15M. All 24 h.

COLL 131

Understanding droplet bridging in ionic liquid-based Pickering emulsions

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We report the experimental work of microparticle self-assembly in ionic liquid-based Pickering emulsions, with emphasis on bridged morphologies, stability, and particle transport. Both the morphology and stability of these emulsions differ greatly from previous work on conventional oil/water Pickering emulsions. The morphology of the previous work showed single, partially or fully covered droplets, while the water/ionic liquid, oil/ionic liquid, and ionic liquid/ionic liquid systems show a high degree bridging of the droplet phase, with the particles avoiding the droplet-continuous phase boundary. The existence of this morphology depends directly on the surface chemistry of the particles. Due to the high free energy of desorption of a particle from a Pickering emulsion interface, conventional oil/water emulsions can experience overall emulsion stability on the order of days or months. However, the emulsions containing bridged structures experience stability on the order of hours due to the large, buoyant bridged structures formed, promoting phase separation.

COLL 132

Anisotropic Sheet-Like Particles: Synthesis and Application as Bulk Rheology Modifiers and Foam Stabilizers

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The large-scale synthesis of anisotropic particles could open the way to a rich variety of new systems of fundamental and applied interest. We present a scalable synthesis technique and discuss the materials applications of a new class of sheet-like particles from ethyl cellulose synthesized by a simple and flexible technique based on liquid-liquid dispersion and anti-solvent precipitation under high shear. The size of the particles is in micrometer range with high aspect ratio. These sheets are hydrophobic and possess interesting properties such as structure modifiers and foam “superstabilizers”. They form intertwined protective shells around the droplets or bubbles. The rheology studies confirmed the extremely strong thickening behavior of the sheets dispersed in non-polar liquids. Only 2.0-3.0 wt.% of sheets were sufficient to convert non-polar liquids to gel-type of systems. Various nano- and microparticles can be incorporated in the polymer sheets. Composite sheets with embedded magnetic nanoparticles respond to magnetic field.

COLL 133

Learning from virus - a facile route to generate core-shell nanoparticles with functional protein corona

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The investigation of protein-polymer or protein-nanoparticle interaction is critical for the development of novel biomaterials and hierarchically assembled nano-architectures. Among them, the polymer-protein core-shell nanoparticles (PPCS-NPs) are the most common structures which offer many advantages in the field of medicine and energy applications. Here we show that PPCS-NPs can be prepared based on synergistic interactions between proteins and synthetic polymers, a strategy learning from virus assembly. This facile and versatile process can yield structural well-controlled core-shell structures, in which proteins stay as the corona and still maintain their original biological activities. A few cases studies will be presented to highlight the application potential of such core-shell nanostructures in drug delivery, antigen presentation and enzymatic reactions.

COLL 134

Theranostic Magnetic Core–Plasmonic Shell Star Shape Nanoparticle for the Isolation of Targeted Rare Tumor Cells from Whole Blood, Fluorescence Imaging and Photothermal Destruction of Cancer

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Theranostic materials are expected to improve early detection and safe treatment through personalized medicine. Driven by the needs, we report the development of a theranostic plasmonic shell–magnetic core star shape nanomaterial based approaches for the targeted isolation of rare tumor cells from whole blood sample, followed by diagnosis and photothermal destruction. Experimental data with whole blood sample spiked with SK-BR-3 cancer cell shows that Cy3 attached S6 aptamer conjugated theranostic plasmonic/magnetic nanoparticles can be used for fluorescence imaging and magnetic separation even in 0.001% mixtures. A targeted photothermal experiment using 1064 nm near IR light at 2-3 W/cm² for 10 minutes resulted selective irreparable cellular damage to most of the SK-BR-3 cancer cells. We discuss the possible mechanism and operating principle for the targeted imaging, separation, and photothermal destruction using theranostic magnetic/plasmonic nanotechnology. After the optimization of different parameters, this theranostic nanotechnology-driven assay could have enormous potential for applications as contrast agent and therapeutic actuators for cancer.

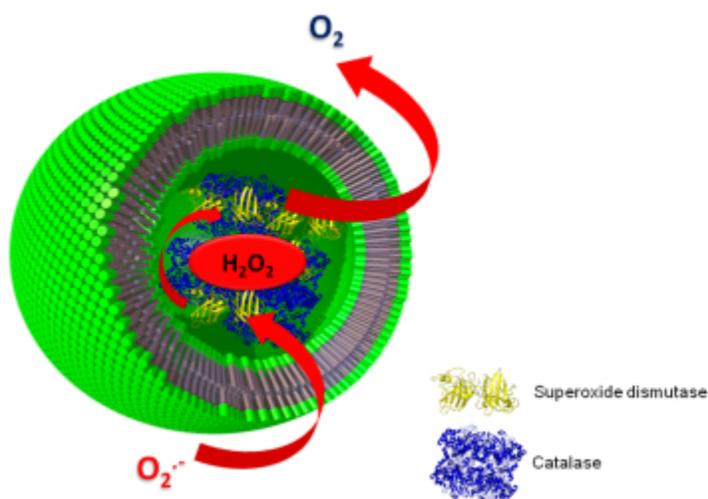
COLL 135

Permeability effects on the efficiency of artificial organelles

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Recently, enzyme-filled polymersomes (nanoreactors) were successfully internalized in living cells. The polymersome permeability is a crucial property, since the membrane must be permeable for small molecules, but impermeable for macromolecules.

We present the implementation of a therapeutically relevant enzymatic cascade in two types of polymersome-based nanoreactors to counteract oxidative stress: superoxide dismutase and catalase. The selected nanocontainers are known to possess different permeability properties. The consequences of these differences regarding the enzymatic activities were investigated by spectrophotometric and electrochemical methods.



COLL 136

Enhancing solubility and stability of curcumin in nanoemulsions

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Phospholipid-based nanotherapeutics, such as the encapsulation of bioactive compounds in microemulsions and nanoemulsions, are gaining popularity as *nutraceutical* delivery systems due to their effectiveness in improving the solubility, stability and bioavailability of the loaded food components. Curcumin, a potential component of Indian diet is not only a potential anticancer but also possesses remarkable antioxidant properties. The paper exploits the formulation of curcumin loaded o/w nanoemulsions by sonication method where ethyl oleate act as oil phase and Tween 80, soy lecithin act as emulsifiers. The particle size and stability of nanoemulsion has been characterized by dynamic light scattering and UV-visible studies. Attempts have also

been made to understand the morphology of loaded nanoemulsion. Efforts have also been made to understand *invitro* digestive release and loading studies. Also, the radical scavenging activity in this nanoemulsion has been found to be 90%. The protein interaction (protein oxidation) with curcumin loaded nanoemulsion has been characterized by fluorescence and FTIR technique.

COLL 137

Fabricating injectable cell/polymer bundles for deep wound repair

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While progress has been made, cellular injection continues to present challenges and is far from being effective in cell-based regenerative medicine. In this study, our goal was to generate small sized (width < 500 microns) and loosely packed polymeric string like scaffolds (i.e. micro bundles) on which cells would grow and, consequently, form injectable cell/polymer bundles for injection into deep wound tissue. The polymeric bundles were fabricated by employing a simple dewetting process under regular cell culture conditions. Induced vascular progenitor cells were seeded on the resulting polymer bundles to grow and form the cell/polymer bundles. The final cell/polymer bundles were able to pass through a syringe needle (gauge 20) with minimal damage to the cells, and a preliminary *in vivo* study indicated that the cell/polymer bundles, as compared to free cells, had better retention of cells in rat myocardium after intramuscular injection.

COLL 138

Shell crosslinked knedel-like nanoparticles for delivery of cisplatin: Effects of crosslinking on cellular response

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Cisplatin is one of the most potent anti-cancer drugs; however, its clinical use is limited due to its severe side effects. We explore the potential of shell crosslinked knedel-like (SCK) nanoparticles as the delivery carriers for cisplatin. Towards this aim, we

synthesized the amphiphilic block copolymer poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS), which was then self assembled into polymeric micelles and subsequently transformed into SCKs by crosslinking the shell domain of the micelles *via* amidation chemistry. These micelles and SCKs contained carboxyl groups in the shell region of the nanostructures, which provided sites for the complexation with cisplatin. Polymeric micelles and SCKs were loaded with up to 48% (w/w) cisplatin. The effects of crosslinking were studied by comparing the release kinetics of these cisplatin-loaded nanoparticles in PBS, stabilities in aqueous milieu, and *in vitro* cytotoxicity in OVCAR-3 ovarian cancer cell lines and RAW 264.7 mouse macrophages of micelles vs. SCKs.

COLL 139

Engineering nanoparticle surfaces for biomolecule conjugation used for protein crystal nucleation and nanoparticle arrangement

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Engineering nanoparticles to self-associate with biomolecules offers a new approach to nucleate protein crystals and create three-dimensional arrangements of nanomaterials. Through adjustment to the polymer molecular weight on a nanoparticle surface the hydrodynamic radius, stability in buffers and interaction with nearby proteins are altered. Large molecular weight poly(ethylene glycol) coatings allow for weak associations between proteins, leading to changes in protein crystallization. In particular, they decrease the time to nucleation, expand the range of conditions for crystal formation and incorporate into the crystal. Composite crystals on the microscopic scale exhibit optical absorbance, fluorescence and super paramagnetic behavior derivative from the incorporated nanomaterials. The arrangement of nanoparticles into three dimensional arrays gives rise to new and interesting properties, such as fluorescence enhancement and varied magnetic response. Application of these results could improve crystallization of traditionally difficult proteins and provide a new matrix to study three dimensional nanoparticle arrays.

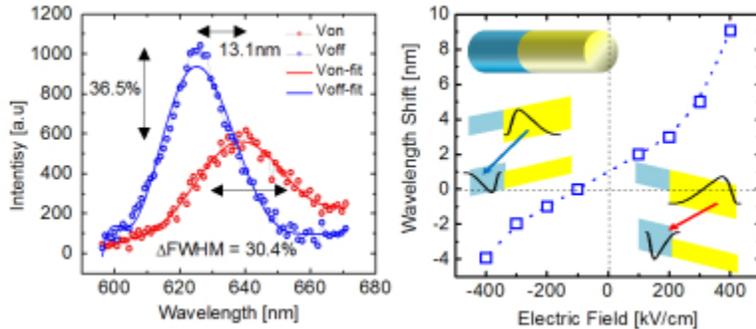
COLL 140

Single Molecule Quantum-Confined Stark Effect Measurements of Semiconductor Nanoparticles at Room Temperature

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We investigate the quantum confined Stark effect (QCSE) of various quantum dots (QD) on the single molecule level at room temperature. It tests QDs' voltage sensing property

for bio & nanoscale application. This study reveals that suppressing the coulomb interaction between electron and hole by asymmetric type-II interface is critical for an enhanced QCSE. In contrast to the well-known quadratic $\Delta\lambda$ -F (wavelength shift-electric field) relation in type-I QDs, asymmetric type-II QDs have roughly linear $\Delta\lambda$ -F relation.



COLL 141

Observation of Potassium Ions in Living HeLa Cells

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Ion pumps control the concentration of ions between the inside and outside of the cell membrane. One of the typical ion pump is 'sodium-potassium pump' that exports sodium ions out of the cell and imports potassium ions into the cell at the same time. As a result, between the inside and outside of the cell the difference of the concentration of sodium ions and potassium ions are formed [1].

In particular, the sodium-potassium pump plays an important role in the stimulation of the nerve cells. The stimulation of the neuron cells is propagated in the form of electrical signals. That signals is formed by action of sodium-potassium pump what controls the states of action membrane potential and resting membrane potential.

In this study, we have measured local concentration of potassium ion in a single HeLa cell using a membrane prepared in glass nano-pipette probe. To observe the potassium ion concentration, we prepared poly(vinyl chloride) (PVC) film with ionophores in a nano-pipette, and the ionic currents were observed using our developed detection system for this study [2]. In case of dead HeLa cells, there was no difference in the ion concentrations between inside and outside of the cell. However, in case of living HeLa cells, the potassium ion concentration was approximately 100 mM higher in the cell than that out of the cell [3].

We will demonstrate the progress of our study in the similar ion concentration measurements in neuron cells.

[1] J. P. Morth et al., Nature, 2007, 450, 1043.

[2] J. W. Son et al., Appl. Phys. Lett. 2011, 99, 033701.

[3] T. Takami et al., J. Appl. Phys. 2012, 111, 044702.

COLL 142

Insight into Antibiotic Resistance of *Pseudomonas aeruginosa* from the Structures of the Outer Membrane Proteins OprG and OprH

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The outer membrane proteins OprG and OprH from *Pseudomonas aeruginosa* have been proposed to contribute to the unusual antibiotic resistance of these bacteria. In order to better understand their mechanism of antibiotic interaction, we have solved the structures of these two proteins by solution NMR spectroscopy. Both proteins form 8-stranded beta-barrels with flexible extracellular loops. Both NMR structures were obtained in DHPC micelles and supplemented with data obtained in lipid bicelles (DMPC:DMPS:DHPC:DHPS 27:9:3:1). The structures were improved by measuring paramagnetic relaxation enhancements. OprH was further shown biochemically and by NMR to interact strongly with lipopolysaccharide through several barrel and loop residues [Edrington JBC286:39211]. This interaction presumably strengthens the OM and reduces its permeability. By contrast OprG appears to form a classic channel for transport of hydrophobic compounds – perhaps including antibiotics – across the OM.

COLL 143

Association of the T-cell antigen receptor ζ subunit with the lipid membrane: Affinities and structure

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The T-cell antigen receptor (TCR) is a cell surface protein complex that initiates immune responses upon interaction with antigens presented by the major histocompatibility

complex. Molecular details of this transmembrane signaling process, in which the cytosolic signaling domain of the CD3-T cell receptor complex, TCR ζ , plays a central role, remain unknown. We characterize the association of TCR ζ with lipid membranes using SPR and neutron reflectometry. The binding of TCR ζ to membranes rich in anionic lipids has a dissociation constant, $K_d \sim 10 \mu\text{M}$. Minute amounts of phosphoinositides, PI(4,5)P₂, increase the affinity by more than 10-fold. NR shows the major portion of the peptide interfacially associated with the bilayer surface and a minor portion penetrating the bilayer deeply. This supports a model in which an α -helical containing ITAMs is aligned parallel to the membrane surface and another α -helical segment is inserted into the bilayer.

COLL 144

HIV-1 Inactivates T-Cells via Interaction Between Membrane Binding Domains of gp41 and the Transmembrane Domains of the T-Cell Receptor Complex: Implications for Therapy of Autoimmune Diseases

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HIV infection is catalyzed by gp41 the envelope protein, which is composed of; the N-terminal fusion peptide (FP), N-terminal heptad repeat (NHR), loop, C-terminal heptad repeat (CHR), pre-TM regions and the transmembrane domain (TMD). Despite extensive studies highlighting important steps in gp41 mediated membrane fusion, the molecular mechanism is not yet fully understood. Furthermore, to successfully infect and replicate, the virus evades immune control by using a broad array of mechanisms, among them the inhibition of CD4⁺ T-cell activity. We deciphered a novel mechanism by which gp41 inhibits T-cell activation via interactions between membrane-bound domains of gp41 and the TMDs of the T-cell receptor (TCR) complex. These include: (i) the FP, which binds specifically to a 9-amino acid motif within the TMD of TCR α subunit and interfere with the assembly of the TMDs. The FP contains a GxxxG motif which is crucial for this interaction. (ii) the TMD of gp41 which we found to include a nine amino-acid motif shared by a group of different viruses, and strikingly resembles the TMD of TCR α . Previous studies have shown that stable interactions between TCR α and CD3 are localized to this nine amino acid motif within TCR α . We found that the gp41 TMD peptide co-localizes with CD3 within the TCR complex and inhibits T cell proliferation *in vitro*. This immunosuppressive activity of gp41 membrane binding domain could be exploited for the design of new therapies for autoimmune diseases.

COLL 145

Topological transitions in membranes, apoptosis proteins, and mitochondrial remodeling

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Bcl-2 family proteins regulate apoptosis by mediating mitochondrial outer membrane permeabilization. They offer potential therapeutic targets to re-engage cellular suicide in tumor cells but an unified understanding of how anti-apoptotic Bcl-xL turns off pores induced by pro-apoptotic Bax remains elusive. Using synchrotron x-ray diffraction and microscopy in cell-free studies, we show that Bcl-xL suppressed not only Bax-induced pore formation, but also membrane remodeling by bacterial toxin and cell-penetrating, antimicrobial and viral fusion peptides, none of which have BH3 domains to mediate direct binding. Furthermore, we show that these Bcl-2 proteins can impact the mitochondrial fission machinery by modifying the local Gaussian curvature of model mitochondrial membranes. Our results are consistent with a conceptual framework in which Bax, Bcl-xL, and lipids interact to produce antagonistic Gaussian membrane curvatures to regulate pore formation. The universal nature of curvature-mediated interactions allows a complementary regulation pathway alongside specific binding.

COLL 146

GpA dimerization in plasma membrane vesicles derived from CHO, HEK 293T, and A431 cells

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Plasma membrane derived vesicles, which bud off mammalian cells upon treatments with chemical or osmotic buffers, allows us to probe membrane proteins without the need for their extraction, purification, and reconstitution. Plasma membrane vesicles can be produced from different cell lines and with different methods, providing us with a rich variety of model systems that are native-like. With the new choices, however, questions arise as to how different the interactions between membrane proteins can be in the different types of vesicle preparations. Here we address this question using Glycophorin A (GpA) as a model. We compare the dimerization of GpA in vesicles derived from CHO, HEK 293T and A431 cells. In addition, we explore the effect of the vesiculation method on GpA dimerization. We show that the cell type and the vesiculation method have a very modest effect on GpA dimerization, not exceeding ~0.8 kcal/mole. The results suggest that the vesicles provide us with a general mammalian plasma membrane model for studies of membrane protein interactions.

COLL 147

Sulfidation and phosphorylation of 30 nm ZnO NPs: Ligand competition and impact on surface charge and solubility

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ZnO nanoparticles (NP) released into the environment can undergo a variety of transformations including sulfidation and phosphorylation. Transformations will alter the NP properties, influencing environmental fate and effects. Here, 30 nm ZnO NPs were sulfidized with S/Zn molar ratios from 0.038 to 2.158, or in the presence of ratios of sulfide and phosphate ranging from 0.06 to 2.2. The resulting speciation was quantified using Synchrotron based Extended X-ray Absorption Fine Structure (EXAFS) and linear combination fitting (LCF), and the particle charge and dissolution rate were measured. From 5% to 100% ZnS was obtained with varying S/Zn ratios. Sulfidation reduced the rate and extent of the release of Zn^{2+} from the NPs; however, the effect was relatively small until the NPs were at least 50% sulfidized (a Zn/S ratio of 0.616). Sulfidation also decreased the zeta potential of the particles, giving them a $pH_{pzc} \sim 7 \pm 0.5$ compared to $pH_{pzc} = 9.1$ for ZnO. ZnS is formed over $Zn_3(PO_4)_2$ when the S/P molar ratio is greater than 0.2, however the ultimate metastable form of the materials depends on the redox state as predicted from thermodynamics.

COLL 148

Effect of monorhamnolipid biosurfactants on the dispersion properties of ZnO nanoparticles

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Metal oxide nanoparticles are quickly becoming ubiquitous in industrial, manufacturing, and medical applications. However, the long-term impact of these nanoparticles on humans and the environment is unknown. One potential route of exposure is dispersion of aggregates into groundwater. Although such nanoparticles are generally hydrophobic in nature, their dispersion in aqueous media may be facilitated by dissolved dispersants such as biosurfactants. Exposure of ZnO nanoparticles to monorhamnolipid (mRL), a biosurfactant, was studied by dynamic light scattering and zeta potential measurements to investigate how pH, surfactant concentration, and time of exposure changed the solution stability of these aggregates. This behavior is further elucidated through mRL adsorption measurements on metal oxide thin films by ATR-FTIR. ZnO nanoparticles quickly aggregate and settle out of solution when no biosurfactant is present, but a portion of the aggregates are solution stable for up to 4 months with only small concentrations of mRL present. Furthermore, an inverse correlation between concentration of solution Zn^{2+} and mRL concentration was observed.

COLL 149

Metal and metal oxide nanomaterials in aqueous environments: A study of size, surface chemistry and other physicochemical properties that impact dissolution and aggregation

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The focus of this talk is on the behavior of metal and metal oxide nanomaterials in aqueous environments. In particular, chemical and physical interactions and properties, including size, surface chemistry and aging, that impact dissolution and aggregation will be presented. These studies combine solution phase quantitative adsorption and solubility studies with molecular-based spectroscopic measurements to provide insights into the dissolution and aggregation behavior of metal-based nanomaterials including ZnO, FeOOH and Cu.

COLL 150

Quantitative analysis of particle-surface interactions in aqueous environments using total internal reflection microscopy

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The detailed interactions of particles with mineral and biological surfaces in aqueous environments determine their ultimate fate and effect. This includes sorption and transport properties as well as toxicity and bioaccumulation. Here we use total internal reflection microscopy (TIRM), which applies state-of-the-art evanescent wave scattering and video microscopy techniques, to track in real time and space different engineered particles (silica and gold) in solution. Quantitative analysis allows us to determine the contribution of forces acting between a particle and a surface, which helps us to calculate important variables such as mean squared displacements, diffusion coefficients, particle size, and their stability over a range of solution conditions (i.e., pH and ionic strength). Findings so far include a better understanding of the silica-water interface and shedding new light on how rod-shaped particles interact with mineral surfaces present in porous media, and with biological surfaces, the latter including phospholipid membranes.

COLL 151

Fate of engineered silver nanoparticles in the environment: Dependence of core size and surface chemistry

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Increased usage of silver nanoparticles (AgNPs) in commercial products underscores the importance of AgNPs fate in the environment. Here a model of engineered AgNPs stabilized with mPEG-SH (MW: 5, 10, 20 and 50 KDa) of sizes 2, 5 and 10 nm was chosen to study dissolution and aggregation that dictate toxicity and stability in various environmentally relevant high ionic strength media such as ¼ th strength hoaglands, hard water, bicarbonate buffer and minimal media. Grafting density of the polymer dominantly directed the dissolution compared to the core size. Larger grafting densities minimized surface oxidation, dissolution rate and prevented aggregation for at least 6 months in contrast to the citrate stabilized AgNPs that crashed immediately after addition of media. Hence, this study implies that different processes in the environment that increase the stability of AgNPs released from commercial products can increase their life time which may have adverse impact on the ecosystem.

COLL 152

Nanoparticle-peptide interactions: Fundamental molecular understanding of the particle-protein interface in aqueous environments

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The increased use of nanomaterials will inevitably lead to their release into the environment. While it has already been demonstrated that nanoscale materials can induce toxicity in a variety of organisms, the mechanisms of such toxicity are only beginning to be addressed. Entry of nanoparticles into biological systems results in the formation of a biomolecular “corona” around the particle. Proteins are an important component of such biomolecular coronas. We are using a molecular in situ based approach to better understand and predict how nanoparticles interact with peptides. As a starting point, we have employed phage display methods to selected peptides that strongly bind with TiO₂ nanoparticles ranging in size from 5 to 20 nm. While the primary peptide sequences yield insight into the types of interactions available to the molecules, we have synthesized labeled peptides to examine the mechanisms of interactions with nanoparticles in aqueous environments by NMR and vibrational spectroscopies. The molecular understanding afforded by this approach offers insight into how nanoparticle binding motifs in proteins may be affected by particle size and composition.

COLL 153

Chemical Transformations of Nanosilver in Biological Environments

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The widespread use of silver nanoparticles (Ag-NPs) in consumer and medical products provides strong motivation for a careful assessment of their environmental and human health risks. Recent studies have shown that Ag-NPs released to the natural environment undergo profound chemical transformations that can affect silver bioavailability, toxicity, and risk. Less is known about Ag-NP chemical transformations in biological systems, though the medical literature clearly reports that chronic silver ingestion produces argyrial deposits consisting of silver-, sulfur-, and selenium-containing particulate phases. Here we show that Ag-NPs undergo a rich set of biochemical transformations, including accelerated oxidative dissolution in gastric acid, thiol binding and exchange, photoreduction of thiol- or protein-bound silver to secondary zerovalent Ag-NPs, and rapid reactions between silver surfaces and reduced selenium species. Selenide is also observed to rapidly exchange with sulfide in preformed Ag₂S solid phases. The combined results allow us to propose a conceptual model for Ag-NP transformation pathways in the human body. In this model, argyrial silver deposits are not translocated engineered Ag-NPs, but rather secondary particles formed by partial dissolution in the GI tract followed by ion uptake, systemic circulation as organo-Ag complexes, and immobilization as zerovalent Ag-NPs by photoreduction in light-affected skin regions. The secondary Ag-NPs then undergo detoxifying transformations into sulfides and further into selenides or Se/S mixed phases through exchange reactions. The formation of secondary particles in biological environments implies that Ag-NPs are not only a product of industrial nanotechnology but also have long been present in the human body following exposure to more traditional chemical forms of silver.

COLL 154

Size- and shape-dependent uptake of silica nanoparticles in *Arabidopsis thaliana*

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The expanding number of commercial products employing nanotechnology warrants the determination of nanomaterial fate, behavior, and potential toxicity in the environment. Silica nanoparticles (SiNPs) in particular have shown increasing prevalence in cosmetic and biomedical applications with researchers evaluating their use as drug delivery vehicles and biolabels. Researchers have started to assess SiNP toxicity to plants, with initial studies clearly indicating that SiNP physicochemical properties play an important role in phytotoxicity and uptake. Herein, we present phytotoxicity and uptake of SiNPs as a function of particle size (i.e., 14–200 nm) and shape (i.e., aspect ratios 1–9) using hydroponically grown *Arabidopsis thaliana* plants. Size- and shape-dependent uptake of the SiNPs by plants was confirmed using transmission electron microscopy (TEM) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Elemental

analysis of the silica confirmed nanoparticle uptake into the roots with minimum translocation into other regions of the plant. Of note, the silica scaffolds were not phytotoxic at the concentrations tested (up to 1000 ppm) despite the significant uptake observed.

COLL 155

Dynamic surfaces: Lipid exchange between nanoparticle supported lipid bilayers (NP-SLBs) and vesicular lipids

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Nanoparticles exist in the environment as the result of natural erosion processes and from man-made materials that find their way into soil/water. Silica nanoparticles can be generated in large amounts from dilute silicate solutions in aquifers, streams, rivers under the influence of acidic conditions (acid rains, acid wastewaters and other industrially-used waters). On the other hand lipids, lipid membranes and lipid degradation products (fatty acids) are ubiquitously present in the environment. As a consequence, SiO₂ nanoparticles often exist with a surrounding supported lipid bilayer (SLB). However, the SLB has a dynamic, not a static structure, and can exchange lipids with other environmental lipid sources. Further, temperature cycling can result in the formation of several bilayers around the nanoparticles and/or the engulfment of SLB aggregates. Here we present nano-differential scanning calorimetry, dynamic light scattering and cryo-TEM data on exchange of zwitterionic lipids between SLBs on nanometer SiO₂ and vesicular lipids.

COLL 156

Concentration-modified polyparameter linear free energy relationships (pp-LFER) for predicting organic compound sorption on carbon nanotubes

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Adsorption of organic compounds on carbon nanotubes (CNTs), governed by interactions between molecules and CNTs surfaces, is critical for their fate, transport, bioavailability and toxicity in the environment. A set of 16 compounds for a multi-walled CNT (MWCNT) and 10 compounds for four different types of MWCNTs were used to develop a new model. This model combines pp-LFER parameters with concentrations to describe the compound-CNTs interactions and to predict the sorption behavior of chemicals on CNTs in a wide range of concentrations (over five orders of magnitude). The pp-LFERs index representing different interactions is found to have a good

relationship with the equilibrium concentrations of compounds. This new approach can successfully interpret the relative contribution of each interaction at a given concentration and reliably predict sorption of various chemicals on CNTs. This approach is expected to help develop a better environmental fate and risk assessment model.

COLL 157

Transport properties and electronic structure of individual metallic nanocontacts on dielectric supports: A local view

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Contacts between metallic nanostructures and semiconducting or dielectric supports are expected to constitute the basic building blocks of future nanoscale electronics and nano catalysts. We investigate with low-temperature scanning probe techniques the transport properties of individual nanocontacts formed between flat metallic islands and their supporting substrates. The observed differential conductance spectra reveal a suppression at small bias voltages characteristic for the presence of dynamical Coulomb blockade phenomena. Calculations based on the theory of environmentally assisted tunneling agree well with the measurements, allowing us to determine the capacitances and resistances of the contacts, which depend systematically on the island-substrate contact area [1]. These findings facilitate quantitative investigations of electrical nanocontacts and are important for future studies of the physical and chemical properties of supported nanostructures in relation to superconductivity, magnetism, and catalysis [2].

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COLL 158

Adsorption of Organic Molecules at Metal and Metal-Oxide Surfaces: Theoretical Challenges, Concepts, and Insights

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Van der Waals (vdW) interactions, level shifts, crossings, electron transfer or electron rearrangements are key elements in the formation of the surface chemical bond. In this talk I will discuss that and how these components act differently for the adsorption of organic molecules at metal and semiconductor (or insulator) substrates.

Examples to be discussed include benzene molecules on (111) surfaces of Ag, Pd, Rh, Ir, and Au, and the adsorption of a strong molecular electron acceptor at semiconductor/insulator metal-oxide surfaces (example: tetrafluoro-tetracyanoquinodimethane, F4TCNQ at ZnO surfaces). For the latter we show that the work function increases notably (up to $\Delta\Phi=2$ eV), even stronger than for the same molecule at metal surfaces. Yet, the cause of this change is qualitatively different at metal and at semiconductor surfaces.

COLL 159

Chromophores at Oxide Surfaces: Energy Alignment, Molecular Packing, and Electronic Pathways

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ZnTPP derivatives are attractive candidates for photoinduced electron-transfer mediators. Using x-ray, UV and inverse photoemission spectroscopies in conjunction with density functional theory (DFT) calculations, we have determined the energy alignment between molecular level and substrate band edges for several ZnTPP derivatives adsorbed on ZnO(11-20) and TiO₂(110) surfaces. Similar energy alignment is found for all of these systems but large differences in solar cells efficiencies, likely due to dye/dye interaction, are observed. We have determined the molecular adsorption geometry of several ZnTPP derivatives at these surface using local and area-averaging techniques. By functionalizing the ZnTPP with phenyl groups in different ways, the molecules adsorb with the porphyrin macrocycle either upright or parallel to the surface. Upright adsorption enables molecular stacking that opens exciton delocalization pathways that compete with direct electron transfer to the substrate. Choosing the appropriate chromophore adsorption geometry is thus critical for electronic charge transfer pathway control.

COLL 160

Interfacial self-organization of organic molecules

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Self-organization of organic molecules is ubiquitous in nature, and also considered a promising route towards technologically relevant materials. In this lecture the deposition and interfacial self-organization of various types of organic molecules is studied in UHV, in solution and in air. The characterization of the resultant structures is done in situ, i.e. within the respective environment, using mainly scanning probe techniques (STM, AFM), complemented by spectroscopic methods like XPS, XPD, and IRRAS. Specific examples include the adsorption of phthalocyanine molecules on a Au(110) surface in UHV, the deposition of viologene and porphyrine molecules on anion-modified copper single crystal electrode surfaces, as well as the self-assembly of long-chain aliphatic alcohols ("wax" -) molecules from Lotus leaves. Besides an understanding of the various systems this lecture aims at an extension of the so-called "surface science approach" to other ambients than UHV.

COLL 161

Interface Chemistry in Carbon-based Nanoelectronics

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In this presentation we review selected interface chemistry issues critical in carbon-based materials and devices. Central to the use of such materials in devices are their reactivity with oxygen, which can strongly affect their energy levels, transport properties, optical response and bonding to other materials. We report on very striking aspects of the light-induced oxidation of crystalline *rubrene*, the highest mobility organic. Although *graphene* is quite unreactive relative to many organic semiconductors, oxidation is one of the best ways to initiate bonding and functionalization, essential in applications. We discuss oxidation chemistries relevant to the exfoliation of graphite to produce graphene. We discuss hybrid *polymer/ZnO* nanostructures, showing how electropolymerization leads to a greatly improved bonding and film interpenetration, especially important in photovoltaic applications. Finally, we present new results on N and P at the *SiC/SiO₂* interface, and its relevance to future devices.

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COLL 162

Hydrogen production from water comparing thermal reactions over reducible metal oxides to photo-catalytic reactions

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Hydrogen production from water is one of the most promising methods to secure renewable sources for energy in general and chemical industry in particular. There are many methods for producing hydrogen from water and these include reducible oxide materials (solar thermal material)[i], combined PV/electrolysis[ii].^[iii] artificial photosynthesis[iv] and photocatalysis[v]. At present about ½ of the total amount of hydrogen produced in the world (about 30 million metric tons/year) is used in the ammonia synthesis process. If humanity can succeed in making hydrogen from water, ammonia and therefore fertilizers will be made from totally renewable sources (nitrogen and water). In this work we are comparing two methods for making hydrogen from water one based on oxidation/reduction cycles of reducible oxides (solar thermal) and the other photocatalytic using Au-Pd/TiO₂ catalysts. The extent of reduction of Ce⁴⁺ to Ce³⁺ has been found to be dramatically enhanced by the incorporation of U⁴⁺ cations within the CeO₂ fluorite structure[vi].^[vii] The reasons for these are at present investigated at the experimental level using core and valence level spectroscopy and computational study using Density Functional Theory with PBE exchange-correlation functional and onsite Coulomb correction (GGA+U) to describe the localized electronic states of Ce ions. Evidence of increased charge localisation around Ce³⁺ cations is seen upon mixing with U⁴⁺ cations as well as a considerable decrease in the oxygen vacancy formation energy. Photocatalytic reactions are also studied where the plasmonic effect of Au together with the synergistic effect of both phases of TiO₂ (rutile and anatase)[viii].^[ix] have resulted in considerable enhancement of hydrogen production.

COLL 163

Single Molecule Spectroscopy of Spin State at Surfaces

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Molecular spin can couple with electrons of metal substrates. Depending on the strength of the coupling spin state of the molecule changes. Examples are given for Iron phthalocyanine (Fe-Pc) adsorbed on Cu, Au and Ag. With strong coupling with Cu(110) the spin is completely killed whereas if decoupled as on Cu(110) 2x1-O, spin survives with change in the direction of easy axis. On Au weak coupling leads to appearance of Kondo state, where a competition between the RKKY interaction affects the spin state. Kondo state of FePc on Au depends on the adsorption site, where the difference was originating from the coupling with the substrate electrons.

COLL 164

Oxidation and reduction of SnO₂ and β-MnO₂ (110), (100), and (101) Surfaces

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Although SnO₂ and β-MnO₂ both crystallize in the rutile structure, the reactivity of their surfaces are very different. For SnO₂, detailed spectroscopic analysis of single crystal surfaces combined with density functional theory (DFT) calculations, have led to a determination of the distinct redox behavior of the (110), (100) and (101) surfaces that is strongly influenced by reduction of Sn⁺⁴ to Sn⁺². For β-MnO₂, however, preparing suitable single crystal surfaces for experimental analysis under UHV conditions has been problematic. Our DFT results indicate that β-MnO₂ surfaces are easily reduced under UHV conditions, and the open d-shell and multiple potential oxidation states of Mn result in many complicated structural changes. These changes are driven by a balance between optimizing d-orbital occupation and minimizing steric and repulsive electrostatic interactions. A number of the predicted reconstructions have not yet been observed for rutile-type oxides.

COLL 165

Molecular interactions between model cell membranes and biological molecules

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Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular interactions between model cell membranes and various biological molecules, supplemented by attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR). Solid substrate supported single lipid bilayers were used as model cell membranes. Protein membrane orientation of G proteins and G protein coupled receptor kinases were quantified. Using SFG, protein complex formation can be observed in situ in real time on model cell membrane.

COLL 166

Identifying the mechanisms for non-random sphingolipid organization in the plasma membrane with secondary ion mass spectrometry

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Sphingolipids and their metabolites serve both as structural components in the plasma membranes of eukaryotic cells, and as bioactive signaling molecules that modulate fundamental cellular processes. Though segregation of the sphingolipids into distinct membrane domains is likely essential for cellular function, the sphingolipid distribution within the plasma membrane and the mechanisms that regulate it are poorly understood. We previously reported that the sphingolipid distribution in the plasma membranes of intact cells could be directly imaged by using high-resolution secondary ion mass spectrometry (SIMS) to map the ^{15}N -enrichment from metabolically labeled ^{15}N -sphingolipids on the cell surface. Our results showed that sphingolipids are enriched within distinct domains in the plasma membranes of fibroblast cells. Here, we use this SIMS approach to investigate the mechanisms that are frequently hypothesized to be responsible for nonrandom lipid distribution within the plasma membrane. The effects of cholesterol depletion, disruption of the cytoskeleton, and obstruction of membrane trafficking on the sphingolipid distribution within the plasma membrane will be presented.

COLL 167

Membrane organization and re-organization probed by imaging mass spectrometry

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We have shown that imaging mass spectrometry using a NanoSIMS can provide high spatial resolution information on the composition of membrane domains in supported lipid bilayers [*Annual Review of Biophysics*, **38**, 53-74 (2009)]. By careful calibration, composition analysis can be made quantitative down to a lateral resolution approaching 50 nm. This method has now been extended to much more complex domains related to canonical raft compositions by isotopic and atom labeling each component in the mixture. In addition, we have reorganized components in the membrane using hydrodynamic flow and observed collective reorganization/co-localization as a probe of membrane lateral interactions relevant to clustering in cell membranes.

COLL 168

Artificial lipid bilayer technology development

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Artificial lipid bilayers are established for studies of reconstituted ion channels and membrane receptors as well as hosting sensors based on engineered pore proteins including potentially DNA sequencing. To expand the scope and use of these applications, we have worked to improve the technological aspects of lipid bilayer

formation and measurement with respect to ease of use, robustness, parallelization, and automation. We have been developing applications of these technologies for measurement of ion channel drug potency and membrane permeability assays. Specifically, we have measured the conductance of TRPM8 and hERG ($K_v11.1$) ion channels in lipid bilayers while perfusing solutions containing drugs at different concentrations, finding its concentration-dependent change characterized by IC_{50} and EC_{50} values. We have been working to measure these channels in parallel and automated bilayer platforms. We have also developed apparatus which allows the artificial bilayers to be stabilized at moderate flow rates, enabling this measurement to be completed in < 10 minutes. We have also developed a microfluidic device which enables the rapid and accurate determination of the membrane permeabilities of chemical compounds. I will report on these results and our current work developing lipid bilayer platforms further.

COLL 169

Real-time observation of molecular transport across cell membranes by second-harmonic scattering and fluorescence microscopy

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Molecular transport at the cellular membrane has been examined in real-time observation conditions by a combination of the surface sensitive technique Second Harmonic Scattering and the Fluorescence Microscopy. Time-resolved second-harmonic scattering (SHS) enables the characterization of the adsorption density as well as transport rates of cationic dyes through living cell membranes.

Dramatically different transport dynamics of malachite-green (MG) and crystal-violet (CV) at *Escherichia coli* (mc4100) and Murine erythroleukemia (MEL) cell have been observed. Both dyes rapidly transport through the outer membrane of *E. coli* whereas only MG, well-known to stain the outer coating of endospores, is observed to penetrate the cytoplasmic membrane. The MG dye on the other hand only adsorbs onto but does not penetrate through the MEL cell membrane. The SHS results are compared with observations made through time-resolved bright-field microscopy experiments in which the overall concentration of the dyes in the cell, including the ones at the membrane and inside the cell, is probed with time-resolution.

The influence of lipid packing in the membrane, presence of ion channels, molecular size and charge, and membrane charge on transport kinetics will be discussed.

COLL 170

Phosphatidylserine asymmetry in lipid bilayers and role of translocation

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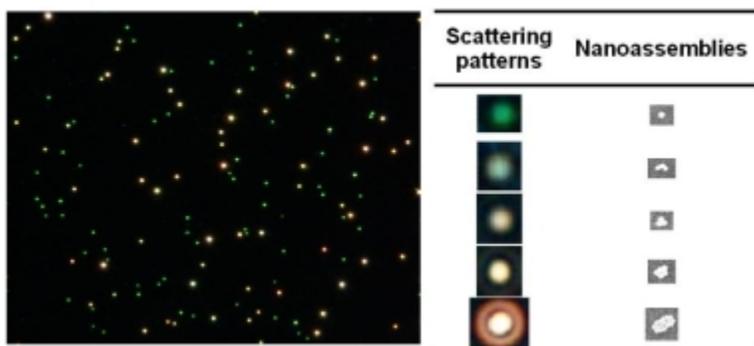
The plasma membrane of eukaryotic cells contains a variety of phospholipids which are not equally distributed between the cytosolic and extracellular leaflets of the membrane. For example, the location of the negatively charged phosphatidylserine (PS) headgroup lipids has drastic effects on cell function, ranging from coagulation to apoptosis. The localization of PS in one leaflet of the membrane is governed by a complex interplay between kinetic and thermodynamic factors. However, the kinetics of PS exchange has not been studied in detail. Sum-frequency vibrational spectroscopy (SFVS) has been used here to measure both the compositional asymmetry and kinetics of PS and phosphatidylcholine (PC) lipid flip-flop in planar supported lipid bilayers composed of 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC) and 1,2-dihexadecanoyl-*sn*-glycero-3-phospho-L-serine (DPPS). The transition state thermodynamics of DSPC and DPPS were measured at biologically relevant compositions ranging from 10 to 35 % DPPS. The activation thermodynamics of DSPC and DPPS and their impact on compositional asymmetry will be discussed in detail.

COLL 171

Localized Surface Plasmon Resonance Shift of Metallic Nanoparticle Assemblies via DNA Hybridization

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Metallic nanoparticles such as gold and silver are known to exhibit localized surface plasmon resonance (LSPR). Being able to form well defined nanoassemblies of metallic nanoparticles in solution phase can produce LSPR coupling and shift, which represents unique plasmon signature and have been used for detection of nanoassembly formation. While most of the existing works focus on nanoassembly formation on a substrate surface, here, we investigated the formation of DNA-modified gold nanoparticle (nAu-DNA) nanoassemblies in bulk solution to study correlations among the LSPR wavelength shift, the plasmon color change, and the nanoassembly structure (Figure 1). We observed that the hybridization percentage of the complementary 50nm nAu increased with rising nAu concentration, longer hybridization time, and longer complementary duplex DNA length. In addition, due to lower scattering yield and smaller surface area from 10nm nAu, the 50nm/10nm hetero-size system displayed limited observable LSPR shift compared to 50nm/20nm hetero-size system, which in turn was inferior to the 50nm/50nm homo-size system. For the hetero-size systems, reducing the surface density of ssDNA on the 20nm and 10nm nAu also significantly reduced the hybridization percentages. Overall, this study allows us to understand how different experimental parameters can impact the assembly of nAu-DNA probes, particularly the limitation in using smaller size nAu (10nm) for LSPR study.



COLL 172

Direct gram-scale chemical synthesis of pure $\text{Ag}_{44}(\text{SR})_{30}$ cluster molecules

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Nanoparticles are currently synthesized with a materials approach, similar to polymer chemistry, wherein the products are only approximately uniform. Ultimately, however, we would like to develop rational strategies to synthesize molecular nanoparticles, similar to organic chemistry. The first two steps have been taken: (i) showing that nanoparticles can indeed exist as molecules, and (ii) showing that single-sized products can be produced by size separations or by destroying less stable species. The latter methods inherently produce small quantities of product. Herein we show that it is possible to directly synthesize gram-scale quantities of $\text{Ag}_{44}(\text{SR})_{30}$ molecules with >90% yield and with no post processing or size separations. These silver cluster molecules are stable for extended periods of time in solid form and in solution in solvents ranging from water to toluene. There appears to be no principle upper limit to the scale of the synthesis, which suggests that kilogram scales of pure product should be achievable.

COLL 173

Catalysis on single Au nanoparticles

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This presentation will describe our work of studying Au nanoparticle catalysis at the single-nanoparticle level with single-molecule imaging techniques. I will present how we interrogate the catalytic activity, mechanism, heterogeneous reaction pathways,

selectivity, and surface-restructuring-coupled temporal dynamics of individual Au nanoparticles. I will also present our latest work in imaging and resolving catalytic reactions on a single nanocatalyst at nanometer resolution, which maps the reactivity of different surface sites and uncovers diverse spatial reactivity patterns at the nanoscale. This spatial resolution of catalysis also enables us to probe communication of catalytic reactions at different locations on a single nanocatalyst, in much relation to allosteric effects in enzymes.

COLL 174

Spatially isolated and highly hybridizable DNA-gold nanoparticle nanoconjugates for biosensing and plasmonic applications

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Conjugates of DNA and gold nanoparticles (AuNPs) typically exploit the strong Au-S chemistry to self-assemble thiolated oligonucleotides at AuNPs. However, it remains challenging to precisely control the orientation and conformation of surface-tethered oligonucleotides and finely tune the hybridization ability. In this talk, I will describe a novel strategy for spatially controlled functionalization of AuNPs with designed diblock oligonucleotides that are free of modifications. We have demonstrated that poly-adenine (polyA) can serve as an effective anchoring block for preferential binding with the AuNP surface and the appended recognition block adopts an upright conformation that favors DNA hybridization. The lateral spacing and surface density of DNA on AuNPs can also be systematically modulated by adjusting the length of the polyA block. Significantly, this diblock oligonucleotide strategy results in DNA-AuNPs nanoconjugates with high and tunable hybridization ability, which form the basis of a rapid plasmonic DNA sensor.

COLL 175

Inorganic nanocrystals as flexible platforms for chemical reactions, sensing and imaging

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Semiconductor quantum dots (QDs) along with metal nanoparticles and clusters exhibit unique photo-physical properties that are not shared by their bulk parent materials. Due to their large surface-to-volume ratios, they provide flexible platforms for arraying various molecules ranging from proteins and peptides to redox active molecules. The emission of luminescent of QDs can be highly sensitive to potential interactions with proximal dyes, metal complexes or metal clusters. We have developed phase transfer approaches to conjugate various biomolecules to CdSe-ZnS core-shell QDs, to Au nanoparticles, and to Au and Ag fluorescing clusters. These were rendered water-

soluble using multi-coordinating polyethylene glycol (PEG)-based ligands presenting one or multiple lipoic acid anchors.

In this presentation, we describe the ligand design and introduce a new phase transfer strategy, based on a photochemically-driven ligand exchange, to promote the dispersion QDs and AuNPs in biological media. We then provide a few specific examples of hybrid bioconjugates and their use in sensor design and biological imaging.

COLL 176

Proximity immobilization of DNA aptamers for protein detection using surface plasmon resonance

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Aptamers are single strand oligonucleotides, either DNA or RNA, sequences. These sequences are selected from very large number of random sequences by an in vitro iterative process, known as SELEX, to bind to the target molecules. Aptamers for metal ions, small organic molecules, proteins as well as whole cells were reported in the literature. It was shown that the binding affinity of aptamers to its target protein is equal and greater than the corresponding antibodies. Hence, currently there has been a great interest to use these artificial antibodies as an affinity reagent in biosensor for protein detection. Earlier we reported a procedure to optimize the immobilization of aptamer on sensor surface, via self-assembly, to increase the specific binding to its target protein, thrombin, and minimize the non-specific adsorption of other proteins. In this presentation we report a procedure, known as proximity immobilization, to imprint two aptamers, which binds at two different binding sites on the thrombin, on the gold surface via self-assembly. This gold surface was used as a surface plasmon resonance sensor surface to detect the protein binding. The resulting biosensor detects protein in the very low concentration range than it is possible to detect using any one of the aptamer biosensor alone.

COLL 177

Surface Enhanced Nonlinear Spectroscopy: Understanding Two-Photon Molecular Properties

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The last decade has seen a resurgent interest in the exploration and utilization of multiphoton processes. Two photon transitions, for example, play critical roles in all-optical switching, biological imaging, and drug delivery via two-photon cleavable lipids.

The intersection, however, of higher-order spectroscopies with the emerging field of plasmonics is an unexplored frontier. Therefore, we have undertaken a systematic study of surface enhanced hyper-Raman scattering (SEHRS), which serves as a prototypical surface enhanced nonlinear spectroscopy. SEHRS demonstrates the ability to probe “dark” electronic states, i.e. those that are inaccessible via one-photon excitation, with extreme sensitivity ($\sim 10^{-10}$ M). It further provides a method to probe the properties of nonlinear chromophores. Such studies have highlighted the importance of non-Condon scattering and suggest new ways to optimize the nonlinear properties of molecules.

COLL 178

One phase growth of highly fluorescent PEGylated and Zwitterion functionalized gold nanoclusters

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We have developed a new one phase synthesis to grow a set of highly fluorescent and multifunctional gold nanoclusters (AuNCs) using reduction of gold precursors in the presence of a series of multi-coordinating ligands made of lipoic acid-appended with either short poly(ethylene glycol) or zwitterion groups. The resulting NCs have a homogenous size, exhibit strong red fluorescence at ~ 750 nm with a quantum yield of $\sim 12-14$ %, and long excitation lifetime of ~ 300 ns. These clusters exhibit remarkable colloidal stability over a broad range of biological conditions. Furthermore, our strategy allowed the in-situ control over the number and type of reactive groups (e.g., COOH, amine, or azide) per NC, making them compatibles with common biochemical conjugations. We will describe the synthetic method along with the optical and structural characterization of these clusters, and discuss their integration in biological hybrids, such as imaging and energy transfer processes.

COLL 179

Remotely-controlled folding of pre-strained polymer sheets into 3D objects

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We discuss the conversion of 2D patterns on pre-strained polymeric sheets that can be folded remotely into 3D objects using an external light source. The pre-strained sheets shrink in-plane when heated uniformly. Here, we use a desktop printer to pattern ink the sheets in specific areas. Those inked regions absorb light preferentially relative to the rest of the sheet and heat up the sheet locally. The resulting temperature gradient across the thickness of the sheet induces gradual shrinkage of the sheet, which results in folding towards the inked side of the sheet. We study thermal shrinkage and rheological properties of polymer sheets under isothermal and non-isothermal heating

combined with thermal transport and finite element modeling. We find that while shrinkage occurs at temperatures above $\sim 100^\circ\text{C}$, significant shrinkage takes place at temperatures $>\sim 120^\circ\text{C}$. We show the folding angle can be determined by invoking both a simple geometric model and mechanical modeling.

COLL 180

Responsive soft materials in confined environments in the presence of external fields.

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In this presentation we will discuss recent advances in the theoretical description of soft materials that are responsive to changes in the environment, such as pH, ionic strength or the application of external fields. One of the systems that we will describe are nanogels formed by block copolymers of polyacid and hydrophobic blocks and the structural changes that occur upon variation in the pH and quality of solvent. The second system will be weak polyelectrolytes grafted on the surfaces of nanopores in the presence of small and large external electrostatic potentials. We will describe the coupling that exists between molecular organization and transport of ions through the pore, with a special emphasis on non-ohmic behavior and the role of pH. The relationship between these systems and biological Nuclear Pore Complex will be discussed.

COLL 181

Optically reconfigurable media enabled by photosensitive surfaces

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Circularly polarized light was employed to write information into cholesteric liquid crystal (CLC) cells that were fabricated with a surface boundary layer comprised of azobenzene-based photoalignment material. CLCs self-organize into periodic helicoidal structures that selectively reflect circularly polarized light of the same handedness as the helices within the CLC film. Nature utilizes similar helicoidal structures for static coloration in the cuticle of beetles and fruit. To move from static to photodriven dynamic optical properties, CLC cells have a number of components (e.g., LC molecules, chiral dopant, substrates, alignment or "buffing" layers, and guest dyes) that may be substituted with (or functionalized to be) photosensitive materials in order to elicit unique responses to light. The effects of boundary conditions imposed by alignment layers on

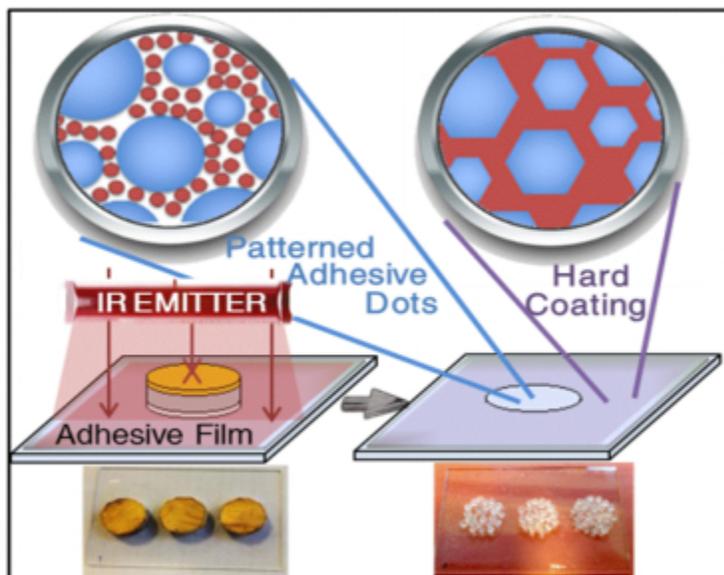
bulk CLC films are considerable. By utilizing a photosensitive material in the alignment layer of a CLC cell, a surface-mediated, light-controlled, reversible and reconfigurable method for patterning a scattering state was demonstrated. Specifically, changes in order/orientation of azobenzene-based material through irradiation with different polarization states of blue/green light induced changes in CLC texture. Such dynamic photodriven response has utility in remotely triggering changes in optical properties, exhibiting passive response to input photostimuli, and in applications where complex spatial patterning is needed.

COLL 182

Large-area patterning of the tackiness of a colloidal nanocomposite adhesive by sintering of nanoparticles under IR radiation

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 (3) Cytec Surface Specialties, Drogenbos, Belgium

We present a simple technique to switch off the tack adhesion in selected areas of a colloidal nanocomposite adhesive layer. In regions that are exposed to IR radiation through a mask, such as gold-coated coins (shown here), the nanoparticles sinter together and harden the adhesive, thus destroying the tack adhesion locally. Adhesive island regions are defined with surrounding regions being non-tacky. The process enables "remote switching" of the adhesive surface at a desired position.



COLL 183

Photoactive Monolayers in Nanoporous Membranes: Applications in Light Activated Switches.

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Nanoscale pores in polymer membranes show great potential for controlled diffusion and other applications. A photoactive monolayer in these nanopores allows closing and opening of the nanopores remotely via UV-visible radiation. Azobenzene thiol molecules were synthesized and adsorbed onto gold-plated, conical pores that were prepared by chemically etching an ion damage tracked polyethylene terephthalate membrane. The ion current across the membrane mounted between two KCl solutions was measured over time at constant voltage. An isomerization of azobenzene thiol in the presence of UV light is accompanied by an observable change in ion current. Grazing angle FTIR studies on monolayers composed of azobenzene thiol mixed in a 1:1 ratio with other thiols were performed to examine the correlation between change in ion current of functionalized nanopores and change in surface dipole of the functional monolayer. Results show that photoactive monolayers are effectual as functionalizing agents in these polymer based nanoswitches.

COLL 184

Programming Smart Macromolecular and Ferroelectric Surfaces for (Bio)Sensing Applications

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We demonstrate the use of electric field induced nanolithography (FINL) to pattern a range of smart polymer brush surfaces: poly(acrylic acid) (PAA), poly(N-isopropylacrylamide) (PNIPAAm), poly(sulfobetaine methacrylate) (PSBMA), and poly(oligo(ethylene glycol) methyl methacrylate) (POEGMA). Our results show that FINL provides a powerful patterning technique that results in the localized topographical and chemical modification of the polymer brush surface only. The resulting chemical modification allows selective addressing of the brush surface with aldehyde reactive coupling chemistries. Furthermore we demonstrate field-induced patterning of surface charge onto ferroelectric thin films (FETFs). We show that FETFs have great potential for biological and interfacial sensing applications in aqueous environments. Specifically, we show that FETF surface charge patterns can be used to control the lateral extent of electric double layer formation in dilute electrolyte solutions, with clear implications for field assisted particle deposition and programmed self assembly.

COLL 185

Morphology modulation of multi-component polymer brushes by patterned surfaces

Marcus Muller, *mmueller@theorie.physik.uni-goettingen.de*, Fabien Leonforte. *Institute for Theoretical Physics, Georg-August University, Goettingen, Germany*

The response of adaptive multi-component polymer brushes to different applied patterned surfaces, as a function of the solvent quality, grafting density of the brushes, and for different sets of parameters related to the applied patterns, is studied in the framework of Molecular Dynamics simulations of a coarse-grained model with soft, non-bonded interactions and implicit solvent. The model is developed in order to address experimentally relevant, large invariant degrees of polymerization, and non-bonded interactions are expressed via a third-order (virial) expansion of the equation of state. The choice of interaction parameters mimics PAA-b-PS diblock copolymer brushes and PAA/PS mixed brushes. The role of the geometry and scale of the surface pattern is explored and related to the response of the inherent selected morphologies of the brushes without confinement.

COLL 186

Polymer brushes with triggered response

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Self-adaptive behavior of mixed polymer brushes has been in the focus of intensive research during the last twelve years. In the classic design, the spontaneous switch of the brush properties occurs when one of the polymers swells up in a selective solvent and occupies the upper stratum of the brush while the counterpart polymer shrinks down. Here we aim to control the switching using an external (or remote) stimulus. In our design we introduce disulfide bonds to the polymer chains forming the brush. Either one or both polymers are cross-linked thus preventing spontaneous reconstruction. However, in the presence of a reducing agent the disulfide bonds are dissociated to the corresponding thiols and the switching is triggered. Such triggered adaptive behavior may open countless possibilities to design novel responsive materials and surfaces.

COLL 187

Surface modification of Nickel nanofibers via polymer grafting

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Â (2) *Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam, New York 13699, United States*

The forests of high aspect ratio (magnetic and conductive) nickel nanofibers were manufactured electrochemically using alumina and polycarbonate membranes. Density of the nickel nanofibers was varied. Next, the polymer brushes were grafted to the surface of the nanofibers using “grafting to” method via surface bound epoxy functionalities. The grafting of the polymer brushes was used to bring functionality to the surface of the nanofibers and prevent nanofibers from permanent sticking. Specifically, we functionalized the head and bottom part of the fibers with grafting of different polymers. As a result hybrid composite nanofibers that can be actuated in external magnetic field with core-sheath morphology have been synthesized.

COLL 188

Nanowire Technology and Terawatt Challenge

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Semiconductor nanowires, by definition, typically have cross-sectional dimensions that can be tuned from 2–200 nm, with lengths spanning from hundreds of nanometers to millimeters. After more than a decade of research, nanowires can now be synthesized and assembled with specific compositions, heterojunctions and architectures. This has led to a host of nanowire photonic and electronic devices. Because of their unique structural, chemical and physical properties, these nanoscopic one-dimensional nanostructures can also play a significant role in terawatt energy conversion and storage. Currently the amount of energy required worldwide is on the scale of terawatts, and the percentage of renewable energy in the current energy portfolio is quite limited. Developing of cost-effective clean technology becomes imperative. I will show two examples from my group, approaching this problem in two different directions. The first relates to saving energy, by developing nanostructured silicon thermoelectrics to do waste heat recovery; and the second, to develop nanostructures for solar energy conversion, either directly to electricity or to liquid fuels through artificial photosynthesis.

COLL 189

Materials for Water-Soluble Electronics

John Rogers, jrogers@illinois.edu. Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, United States

A characteristic feature of modern silicon integrated circuit technology is its ability to operate in a stable, reliable fashion, almost indefinitely for practical purposes. Recent work demonstrates that carefully selected sets of materials and device designs enable a class of silicon electronics that has the opposite behavior -- it physically disappears in water or biofluids, in a controlled manner, at programmed times. This talk summarizes recent work on this type of 'transient' electronics technology, ranging from basic studies of dissolution of the key materials, to development of components and systems with

radio frequency operation, to invention of schemes for externally 'triggering' transient behavior.

COLL 190

Charge transport across self-assembled monolayers

George Whitesides, *gwhitesides@gmwgroup.harvard.edu*, *Hyo Jae Yoon, Felice Simeone, Jabulani Barber, Martin Thuo*. *Department of Chemistry and Chemical Biology, Harvard University, United States*

Charge transport by tunneling across thin films of “insulating” organic matter is important in a number of biological processes (photosynthesis, respiration, many redox processes), and relevant to understanding charge transport in organic matter in organic electronics. We are developing a system for studying the physical-organic chemistry of charge transport across SAMs sandwiched between two metal electrodes: one silver (or gold), and the other a low-melting eutectic alloy of gallium and indium (“EGaIn”) with a surface film of Ga₂O₃. This junction is providing detailed (and in some instances, puzzling) information about current densities and rectification in this junction, and especially about the role of the SAM, the influence of the structure of the molecules in the SAM and the tunneling current, and the structure of the interfaces of the SAM with the electrodes. This talk will describe this system, discuss its strengths and weaknesses, and summarize results obtained using it.

COLL 191

Hollow and nested nanocrystals as catalytic nanoreactors

A. Paul Alivisatos, *APAlivisatos@lbl.gov*. *Department of Chemistry, Univeristy of California, Berkeley, Berkeley, CA 94720, United States*

We are developing new routes to prepare hallow nanocrystals and nested nanocrystals. In these routes, it is possible to selectively control the wall thickness and porosity. We are exploring the use of these multi-component nanocrystals on catalytic systems with enhanced properties compared to more common topologies where a catalytic particle rests on an open support.

COLL 192

Metal nanoparticle catalysts: effects of particle size and support on metal atom energetics, catalytic activity and sintering rates, and why these correlate

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Many important catalysts for energy technology involve late transition metal nanoparticles dispersed across the surface of some support. The relationships between the energetic stability of late transition metal particles on oxide supports and their structural, electronic, chemisorption and catalytic properties will be reviewed. Oxide-supported metal catalysts have been studied here using well-defined surfaces involving vapor-deposited metals on single-crystal oxide surfaces, where the metal atoms nucleate and grow nanoparticles. The energetic stability of the metal atoms in these nanoparticles has been measured as a function of particle size and support by metal atom adsorption calorimetry. Their small-molecule chemisorption properties and sintering kinetics have also been measured. We find correlations amongst the energetics of the metal atoms in nanoparticles, which depend both on their particle size their oxide support, and the strength with which they bond adsorbates, catalytic kinetics and sintering rates. * Work supported by DOE-OBES Chemical Sciences Division.

COLL 193

Crystallization, slow dynamics and kinetic arrest in dense suspensions of Janus and uniaxial colloids

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The rich bulk self-assembly behavior of amphiphilic Janus colloids of variable patch number, size and shape is studied using nonperturbative self-consistent phonon theory. The coupled translational and rotational contributions to the free energy and localization parameters are determined as a function of crystal symmetry, thermodynamic state and patch orientational order. In two-dimensions, diblock Janus colloids can form striped, modulated striped (zig-zag) and plastic crystals, and the phase diagram depends sensitively on Janus balance, temperature and pressure. Calculations for triblock Janus particles have also been performed. Coupled translation-rotation activated dynamics in dense fluid suspensions of homogeneous and Janus dicolloids that interact via short-range attractions have also been studied using nonlinear Langevin equation theory. For larger aspect ratios, there is strong translation-rotation coupling, and repulsive glasses, gels and attractive glasses can form. For small aspect ratios, plastic glasses emerge, and translational and rotational motion strongly decouple leading to two-step relaxation.

COLL 194

Dielectric Effects in the Self-Assembly of Binary Colloidal Mixtures

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Colloidal self-assembly is often controlled by electrostatic interactions. If the colloids have a dielectric constant that is different than the dielectric constant of the solvent,

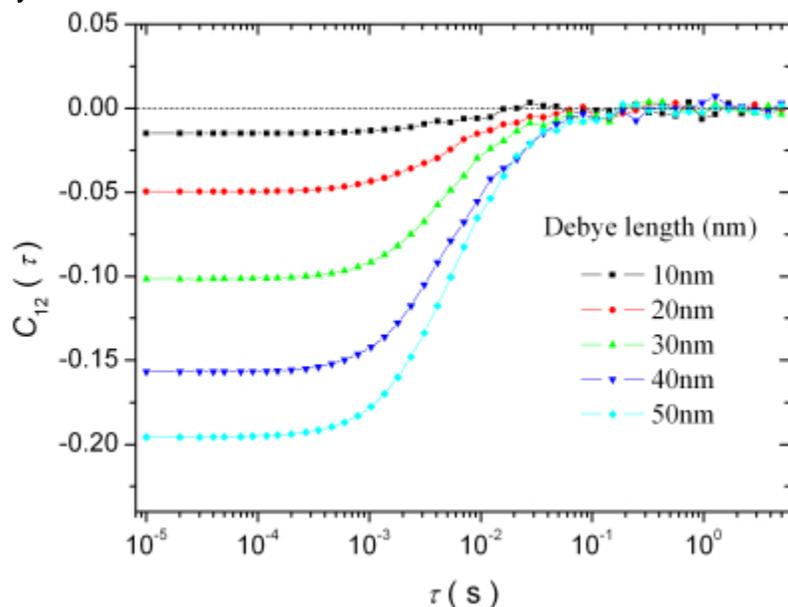
polarization charges are induced at their surface. Despite the large dielectric mismatch encountered in typical colloidal suspensions, the computational complexity of this problem causes the resulting many-body effects to be generally ignored in theoretical as well as computational studies. To remedy this situation, we introduce an efficient method that properly accounts for polarization charge and apply it to study colloidal self-assembly in binary mixtures via molecular dynamics simulations. We demonstrate that variation of the dielectric contrast can qualitatively alter the nature of the aggregation.

COLL 195

Simulating number correlation function of interacting colloidal system: a Brownian Dynamics Study

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This study focuses on the correlation between the dynamics of individual particles in a dense charged colloidal system. By Brownian Dynamics simulation, the negative number correlation function of these interaction colloids are calculated, which, by further theoretical analysis, help to extract information of the diffusion rate of the individual colloids (at difference time scale) and the interacting length scale between the particles. The simulation provide an effective approach of interpreting the results of multi-color fluorescence correlation spectroscopy, which allows particle recognition within a dense system.



COLL 196

Core-Shell Composite Particles – Synthesis, Characterization, and Application

Lenore L. Dai, *Lenore.Dai@asu.edu. School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, Arizona 85287, United States*

Nanoparticles are receiving increasing attention since they have properties that are significantly different than those of bulk materials. Organic-inorganic composites are vital in biological, medical, and chemical applications. Among them, core-shell composite nanoparticles are a unique class of materials which are attractive for their potential applications as delivery vehicles (for drugs, dyes, cosmetics, ink etc.). In this presentation, we report the synthesis of core-shell composite nanoparticles through one-step Pickering emulsion polymerization. The polystyrene/poly(N-isopropylacrylamide) (PNIPAAm)-silica core-shell nanoparticles are temperature sensitive, demonstrate effective drug release upon volume change, and show promising cytotoxicity results in prostate cancer therapy. The thermal transition temperature can be tuned by incorporating additional co-monomers, co-solvents, and ionic surfactants. In addition, we have successfully synthesized polystyrene/poly(N-isopropylacrylamide)-gold core-shell and asymmetric composite particles.

COLL 197

An Extremely Robust Strategy for Functional Nanocrystals

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In this presentation, we report on an extremely robust strategy for crafting a large variety of functional nanocrystals with precisely controlled dimensions (i.e., plain, core/shell, and hollow nanoparticles) by capitalizing on a new class of amphiphilic *unimolecular* star-like block copolymers as nanoreactors.

COLL 198

Janus colloids and beyond

Qian Chen, *qchen@berkeley.edu. Department of Chemistry and Miller Institute for Basic Research in Science, University of California- Berkeley, Berkeley, California 94720, United States. Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

We develop general guidelines for the rational design of both building blocks and interaction patterns of patchy colloids in liquid suspension, towards the long-term goal of developing the practical capability to make a colloidal structure, or any colloidal material, that is "assemblable". Two levels of efforts are included in this talk, first, the fabrication of patchy colloidal particles on demand, second, the observation and analysis of their self-assembly dynamics. A collection of theoretical calculation, dynamic simulation, and experiments is shown to demonstrate phase diagram construction and

kinetic pathway selection. We rely throughout on the capacity, in these colloidal systems, to resolve the motions of individual particles in suspension by optical microscope. This work was done in Steve Granick's group, in collaborations with Erik Lijten and Xiaoming Mao.

COLL 199

Glassy dynamics under confinement

*Krishnan S. H.^{1,2}, **Ganapathy Ayappa**¹, ayappa@chemeng.iisc.ernet.in. (1) Department of Chemical Engineering, Indian Institute of Science, Bangalore, Karnataka 560012, India (2) Current Address: Samsung Advanced Institute of Technology India Group, SISO Pvt.Ltd., Bangalore, Karnataka 560093, India*

A glass is formed, when a liquid is rapidly cooled below its melting point. Unlike a liquid, a glass is typically amorphous with characteristically slow atomic mobilities

and higher viscosities. Although many materials such as polymers and silicates readily form glasses

upon cooling, simpler monoatomic rare gases

do not readily form glasses, since they prefer to pack into the crystalline phase. Thus forming a glass with these simple single component fluids has been elusive.

In this work, we show that the non-glass forming nature of monoatomic rare gases can be overcome by confining the fluid between two infinite flat surfaces at nanometer separations. Using molecular dynamics simulations we observe the characteristic slowing down of the particle displacements and power law dependence

of relaxation times as the system is cooled. These observations conform to mode coupling theory predictions, a dynamic theory used extensively to characterize the glassy state.

Upon continued cooling we observe three distinct slow relaxations associated with a partially crystalline state of the trapped fluid.

In addition to improving our understanding of the dynamic slowing down during glass formation, the implications of the study in determining the state of fluids under extreme confinement such as the surface force apparatus will be overviewed.

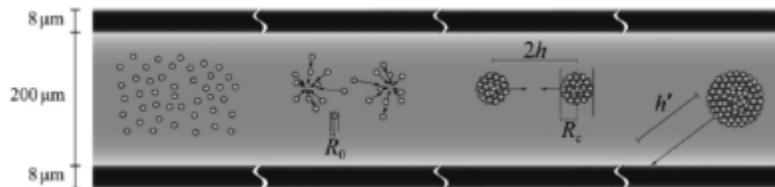
COLL 200

High-speed photography of encapsulated microbubbles

*Spiros Kotopoulos, **Michiel Postema**, michiel.postema@ift.uib.no. Department of Physics and Technology, University of Bergen, Bergen, Norway*

The ultrasound-induced formation of bubble clusters may be of interest as a therapeutic means. If the clusters behave as one entity, i.e., one mega-bubble, its ultrasonic

manipulation towards a boundary is straightforward and quick. If the clusters can be forced to accumulate to a microfoam, entire vessels might be blocked on purpose using an ultrasound contrast agent and a sound source. We analyse how ultrasound contrast agent clusters are formed in a capillary and what happens to the clusters if sonication is continued, using continuous driving frequencies in the range 1–10 MHz. Furthermore, we show high-speed camera footage of microbubble clustering phenomena.



COLL 201

High-speed fluorescence imaging of the US-triggered release from liposome-loaded microbubbles

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Many examples of the therapeutic application of ultrasound contrast agents microbubbles have emerged in the last couple of years. Various microbubble designs have been shown to be capable of carrying drugs to a specific region in the body and enhancing the uptake or delivery efficacy, in particular when drugs are loaded into liposomes and attached to the surface of the microbubbles [2]. Although the therapeutic effect has been shown, the physical mechanism behind it has not been fully clarified. An essential step in the process of triggered drug delivery is the release of a drug from the bubble surface. The release takes place at a microseconds timescale and the drugs or drug-carrying vesicles (order 200 nm) are too small to resolve with a standard microscope. Thus, it is an extremely challenging task to visualize these processes. Here we use high-speed fluorescence imaging to visualize the ultrasound-triggered release from fluorescently labeled liposome-loaded microbubbles at a frame rate of 100,000 frames per second.

COLL 202

Encapsulated microbubbles for contrast ultrasound imaging and targeted drug delivery: Interfacial rheology of the encapsulation

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Micron-size gas bubbles encapsulated by a nanometer layer of lipids, proteins and surfactants are injected into a patient's body to improve ultrasound imaging. We are the first to propose and subsequently develop an interface model of the encapsulation--has

an intrinsic surface rheology with surface viscosities and elasticities--that addresses the wide disparity of scales between the bubble size and that of the encapsulation. I will discuss material characterization of these contrast agents that includes determination of rheological properties of a contrast microbubble's encapsulation using one set of in vitro experiments, followed by model validation using another set. I will present a hierarchical approach with increasing sophistication in constitutive modeling of the encapsulation as warranted by the determining experiments and underlying physics. I will discuss subharmonic signals used for noninvasive monitoring of organ-level blood pressure, and explain their unusual behaviors in sharp contrast to "plausible expectations" and classical bubble dynamics results.

COLL 203

Interpreting interfacial dilatational rheology of an oscillating microscale bubble

Shelley L. Anna, *sanna@cmu.edu*, **Anthony P. Kotula**, *Center for Complex Fluids Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

While numerous techniques have been developed to probe interfacial rheology, such methods are riddled with practical difficulties and a lack of understanding of how to interpret the measurements. For dilatational rheology, only methods involving purely spherical interfaces achieve purely dilatational deformation. These analyses commonly assume the Laplace equation describes the pressure jump across the oscillating interface, but this does not account for deviatoric stresses arising when an interface is deformed. Here, we derive the surface stress on an oscillating microscale spherical bubble, accounting for Marangoni and Gibbs stresses, transport, and intrinsic rheology, demonstrating that each behavior contributes separately. We compare several measurement methods, including a microtensiometer that we developed. We show that the measured dilatational modulus can depend on geometry and is not a material property in itself. Thus, interpretation must be undertaken carefully.

COLL 204

Nesting microbubbles: Influence on inertial cavitation, imaging, and cell death

Steven Wrenn¹, *spw22@drexel.edu*, **Stephen Dicker**¹, **Alexandra Bartolomeo**¹, **James Dierkes**¹, **Nily Dan**¹, **Michal Mleczko**², **Georg Schmitz**².¹ *(1) Chemical & Biological Engineering, Drexel University, Philadelphia, PA 19104, United States* ² *(2) Medizintechnik, Ruhr University, Bochum, North Rhine - Westphalia 44801, Germany*

This talk reviews a microbubble construction in which one or more phospholipid-coated microbubbles are nested inside the aqueous core of polymeric microcapsules. The microbubbles comprise a sulfur hexafluoride gas core, stabilized by a distearoylphosphatidylcholine surfactant monolayer containing up to 8 mole% poly(ethylene glycol) tethers to prevent coalescence. The microbubbles, which range in diameter from nominally 0.5 – 2.5 microns, are further nested inside water-filled,

poly(lactic) microcapsules with diameters of nominally 5 microns. Nesting prolongs microbubble longevity – from minutes to hours - upon exposure to ultrasound, raises – by as much as a factor of three - the peak negative pressure required for inertial cavitation, and essentially eliminates cell death – irrespective of pressure - in close proximity to cells. The method of nesting will be presented, along with results from inertial cavitation experiments, CaCo-2 human epithelial colorectal adenocarcinoma cell death studies, and temporal measurements of contrast-to-tissue ratios in gel phantoms.

COLL 205

Physical chemistry of lipid/lipopolymer shelled models of medical microbubbles

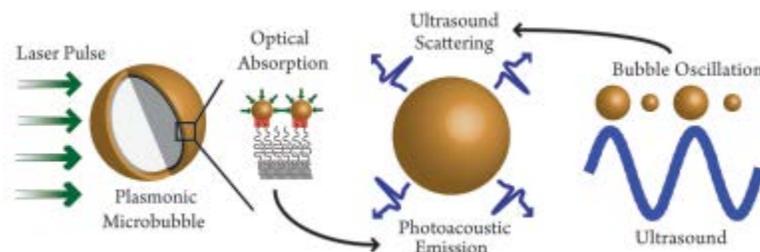
Marjorie L Longo, *mllongo@ucdavis.edu*. Department of Chemical Engineering and Materials Science, University of California Davis, Davis, CA 95616, United States

In this talk, I will reflect upon my group's investigation of the richness of physical chemical behavior in microbubble shells resembling the lipid/lipopolymer shells of certain medical microbubbles. These findings will then be related to understanding and engineering the performance of microbubbles.

COLL 206

Plasmonic Microbubbles as Dual Mode Contrast Agents with Enhanced Photoacoustic Generation

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To fabricate the plasmonic microbubble, biotin functionalized, lipid-coated microbubbles were decorated with 5-7 nm gold avidin-nanospheres to generate gold nanoparticle-coated microbubbles (AuMBs). Multiphoton luminescence microscopy and inductively coupled plasma mass spectroscopy confirmed the loading of the gold nanoparticles onto the microbubbles. Ultrasound images were produced from a flow-through phantom and confirmed the AuMBs remained acoustically active. The photoacoustic response of the AuMBs was characterized and a significant enhancement over free nanoparticles was observed.

COLL 207

Influence of Fabrication Method on Functional Properties of Microbubble Agents for Theranostic Applications

Graciela Mohamedi¹, *graciela.mohamedi@eng.ox.ac.uk*, **Neveen A Hosney**², **Paul Rademeyer**¹, **Yoonjee Park**³, **Joshua Owen**¹, **Tuan Pham**³, **Joyce Y Wong**³, **Marina Kuimova**², **Eleanor Stride**¹.^Â (1) Department of Engineering Science, University of Oxford, Oxford, United Kingdom^Â (2) Department of Chemistry, Imperial College London, London, United Kingdom^Â (3) Department of Biomedical Engineering, Boston University, Boston, MA 02115, United States

Suspensions of surfactant stabilized microbubbles are used clinically as ultrasound imaging contrast agents. They have been widely investigated as drug delivery vehicles and recent work has demonstrated their potential as multi-modality theranostic agents. Extensive studies have been made of the effects of the coating material and the gas core on microbubble characteristics but not of the effects of the processing method. The aim of this work was to investigate the latter.

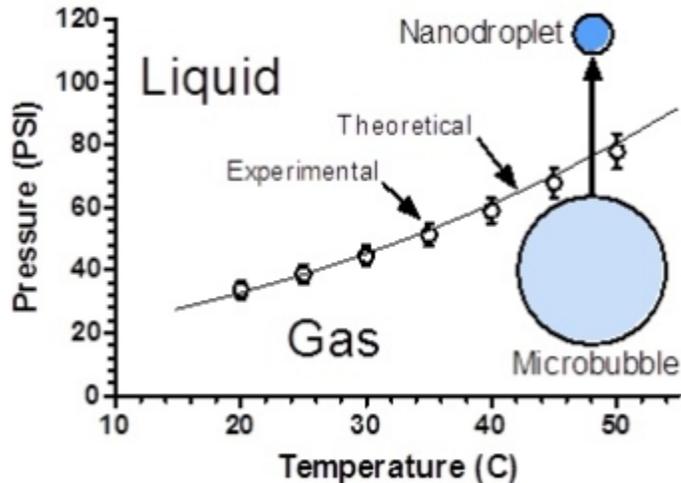
Surfactant coated microbubbles were produced using either sonication or in a specially designed microfluidic device. The microstructure of the bubbles was observed using fluorescence lifetime imaging (FLIM), and environmental SEM. The method of bubble generation was found to significantly affect the characteristics of the bubble surface, bubble stability and their acoustic response. The results demonstrate that the processing method affects not only the bubble size distribution but also other characteristics important for biomedical applications.

COLL 208

Thermodynamics of perfluorocarbon microbubble phase-change agents

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Microbubbles for contrast enhanced ultrasound imaging are limited to intra-vascular transport because of their size (1-10 μm) relative to gaps in the endothelial wall (e.g. 100-750 nm in leaky tumors).¹ Phase-change-agents (PCAs) utilize a liquid-to-gas phase change to convert a nanodroplet capable of extravasation to a microbubble, which provides ultrasound contrast. Methods to produce PCAs include microbubble condensation.² To better understand the thermodynamics of PCA behavior, we have constructed experimental pressure-temperature condensation phase diagrams.



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COLL 209

Nanoscale design of self-cleaning surfaces that manipulate and kill bacteria

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In contrast to materials that release compounds that kill bacteria, contact antimicrobial surfaces do what they sound like: they kill the bacteria that they touch. Contact antimicrobial surfaces are therefore economical from the perspective of expensive antimicrobial compounds, with the additional benefits of minimal toxicity and a lack of dosing issues (or depletion of compound with time.) A challenge, however, is that the cationic functionality necessary to ensure intimate microbe-surface contact and to afford killing is responsible for retention of dead bacteria, which then form a breeding ground for further biofilm growth. Here we investigate the utility of clustering cationic charge in nanoscale elements: By concentrating adhesive and antimicrobial functionality on otherwise nonadhesive surfaces we demonstrate selective bacterial capture, surprisingly high killing efficiencies at low levels of functionalization, and bacterial

release. The possible mechanism, especially in terms of charge density and surface topography are further explored.

COLL 210

Anti-bioadhesion on Hierarchically Structured, Superhydrophobic Surfaces

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We have successfully prepared hierarchically structured, superhydrophobic surfaces, with single-, dual-, and triple-scale roughness, via a layer-by-layer (LbL) particle deposition approach. The dual-/triple-scale structured surfaces demonstrated more pronounced water repellency than their single-scale counterpart. These superhydrophobic surfaces, especially the triple-scale structured surface, exhibited significantly reduced protein adsorption. The superhydrophobic surfaces can also markedly reduce platelet adhesion and activation; in particular, platelet adhesion was completely suppressed on the triple-scale structured surface. By synergistically tuning surface chemistry and topography, the hierarchically structured surfaces may become an attractive platform for a range of biomedical applications.

COLL 211

Thiol-reactive self-reporting surface as template for biomolecules

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Simple and easily accessible methods to fabricate versatile multi-protein arrays with control not only over the specificity of the immobilization but also over the orientation of each of the immobilized proteins are in great demand in nanotechnology and life sciences.

Reactive and fluorescent reporter monolayers, i.e. monolayers that have some reactive moiety at the head-group that allows simultaneous anchoring and visualization of the product of immobilization, are extremely useful for (bio)molecular (nano)fabrication.

The current presentation focuses on a new strategy for the simultaneous detection and immobilization of thiols. An orthogonally modified coumarin has been used to fabricate a fluorogenic reactive monolayer platform on glass, for the covalent and selective immobilization of thiols. The platform properties in terms of reactivity, selectivity, sensitivity and co-localization towards thiols have been assessed. Adopting multifunctional orthogonal covalent and non-covalent immobilization strategies we demonstrate the direct oriented ligation of proteins onto the self-reporting fluorogenic reactive monolayer.

COLL 212

Comparative study of protein adsorption, conformation, and binding at PEG and PolySBMA interfaces

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Hydrophilic poly(ethylene glycol) (PEG)- and zwitterionic poly(sulfobetaine methacrylate) (pSBMA)-based materials have been widely used in drug-delivery systems due to their super-lowfouling capacity. However, molecular interactions between proteins and these two polymers remain elusive, although both polymers can achieve similar antifouling performance. Here, we develop systematic ways to examine and compare the conformational changes and surface binding of different proteins (BSA and Lysozyme) upon interacting with PEG and pSBMA materials using multiple spectroscopic techniques including NMR, AFM, SPR, and ATR-FTIR. It was observed that polymer-induced conformational change of proteins affects the activity and binding of adsorbed proteins. Additionally, we also investigate the effects of polymer molecular weights and polymer concentrations on protein-polymer interactions. This work provides new insights into the fundamental understanding of protein-polymer interactions underlying protein catalysis, protein engineering and design, and protein drugs.

COLL 213

Design & fabrication of a 3D pillar electrode array for transduction of retinal responses

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In the past several decades there has been a tremendous effort in the development of hybrid biological-electronic sensor systems that allow a more comprehensive understanding of the retina. Current techniques of neural sensing employ electrode arrays that are typically large in size and utilize direct current measurements, leading to limited resolution and retinal tissue damage. The work presented here shows a novel sensing approach and development of a prototype device that relies on capacitive coupling between unique 3D semiconductor electrode probes and neural tissue to measure electrical activity in the retina due to light stimulation. Specifically, design and microfabrication of the semiconductor device is described and interfacing of this device

with retina is demonstrated. The work being presented provides a base for implementation of semiconductor probe technologies in robust (bio)molecular sensing devices that study the dynamic function of retinal-neuronal networks.

COLL 214

Laser light scattering measurement of polymer directed calcium phosphate biomineralization

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Polyelectrolytes and proteins containing acidic moieties, such as carboxylate, are important in biomimetic calcium phosphate (CaP) mineralization during bone/teeth formation. However, the precise role of charged polymers remains elusive largely due to experimental difficulties associated with measuring transient nanostructures. This study combines dynamic and static laser light scattering to determine how two polymers containing pendent carboxylate functionalities direct aggregation and subsequent assembly in collagen matrix. We show that the polymer structure can alter the CaP aggregation mechanism, whereas the polymer concentration strongly influences the rate of CaP aggregation. These results provide important cues for bottom up assembly of polymer directed CaP biominerals.

COLL 215

A click-switch for cell adhesion, migration or shape change

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We present a readily accessible strategy for creating protein-resistant surfaces that contain azides, based on spontaneous adsorption of a comb-like copolymer. Using a strain-promoted azide alkyne cycloaddition, we illustrate the single-step conjugation of various representatives of important applications: the labeling with small organic molecules, capture of nanoparticles, attachment of native enzymes at a controlled density, and control of cell adhesion. Through the simple addition of a functional peptide to cell culture medium, our substrates' cell-adhesive properties can be switched on demand, allowing dynamic studies. This powerful technique allowed diverse applications. We demonstrate rapid cell adhesion following peptide addition, and studied triggered spreading using various cell lines. Experiments were performed at the single cell level, but also on the collective level. Using pattern-in-pattern techniques, we explored substrate-wide triggered cell shape change and patterned coculturing as promising applications of this versatile yet accessible strategy.

COLL 216

Reactive Monolayers: Templates for Biomolecules and Interfaces for Technology

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Self-assembled monolayers have been the workhorse for nanotechnology since a few decades. They constitute an interface and “interphase” between a substrate and the “outside world”. Their functions have progressed into ever increasing added value including molecular recognition, molecular construction, biomolecular orientation, electronic transport, signalling, etc.

Reactive monolayers, i.e. monolayers that have some reactive moiety at the headgroup that allows further functionalization, form a subclass that is extremely useful for molecular (nano)fabrication. The reactivity of such monolayers can be the same or drastically different than of their solution analogs.

The current presentation focuses on examples that range from biomolecular templates to technological applications. The development of reactive platforms that signal attachment reactions occurring onto them is useful for biomolecular arrays. Examples will be shown of protein patterns, using a thiol-reactive platform. Surface gradients are being developed and used to address and map reactivity profiles on surfaces on reactive monolayers.

COLL 217

Multilayering of pseudo-polyelectrolytes

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The use of weak polyelectrolytes in multilayer polymer systems provides a means of altering the physicochemical properties of these thin films. We have examined the limits of the polyanions by incorporating the pseudo-polyelectrolytes (pPE), poly(4-vinylphenol) (PVPh), into multilayer systems with either the weak polyelectrolyte (WPE), poly(allylamine hydrochloride) (PAH) and the strong polyelectrolyte (SPE), poly(diallyldimethylammonium chloride) (PDADMAC). Since PVPh exhibits moderate antimicrobial ability, we tested these multilayered systems to determine their antimicrobial profile. For the PDADMAC/PVPh coatings, >70% inhibition of growth of *S. epidermidis* was observed at an assembly pH of 10.5 and 11.0. We have also been able to exploit the lowered pKa of the alcohol, poly(norbornenylhexafluoroisopropylmethyl alcohol) (HFIPA), and successfully multilayered with both PAH and PDADMAC. These films are remarkable thick and are very hydrophobic. We have also introduced another pPE into this field; poly(4-vinylbenzeneboronic acid) (PVBBA), which is being evaluated as part of a breathalyzer apparatus for diabetes.

COLL 218

pH-Dependent interfacial refolding and transmembrane insertion of proteins

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The conversion of a protein structure from a water-soluble to membrane-inserted form is one of the least understood cellular processes. Examples include the cellular action of various bacterial toxins and colicins, tail-anchor proteins and multiple proteins of the Bcl-2 family, regulating apoptotic response in the cell. In our lab we study diphtheria toxin (DT) T-domain, which undergoes conformational change in response to endosomal acidification, inserts into the lipid bilayer and translocates its own N-terminus and the attached catalytic domain of the toxin across the membrane. Our goal is to describe at the molecular level the mechanisms of acid-induced conformational switching of the DT T-domain, which serves as a model for membrane insertion/translocation transitions of structurally related proteins. Here we present our progress toward this objective, including structural, kinetic and thermodynamic characterization of the insertion pathway of the DT T-domain using various spectroscopic tools (FCS, FRET, fluorescence lifetime quenching, CD etc.). We compare the mechanism of pH-triggered membrane insertion of the T-domain, to that of the anti-apoptotic regulator BCL-XL, which has a similar solution fold. Supported by NIH GM069783.

COLL 219

Assembly of functional high density lipoprotein

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High density lipoprotein (HDL) associated paraoxonase-1 (PON1) is crucial for the anti-oxidative, anti-inflammatory, and anti-atherogenic properties of HDL. Discoidal apolipoprotein (apo)A-I:1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) complexes have been shown to be most effective in binding PON1, stabilizing it, and enhancing its lactonase and inhibitory activity of low density lipoprotein (LDL) oxidation. Human apoA-I contains 243 amino acids. Based on our earlier studies demonstrating that apoA-I mimetic peptide 4F forms discoidal complexes with lipid, we hypothesized that lipid complexes of 4F would be able to bind PON1, increase its stability, and improve its activity. To test our hypotheses, a recombinant PON1 was expressed in *Escherichia coli* and purified. Our preliminary studies with rPON1 have shown significant increase, compared to the control, in the paraoxonase activity in the presence of 4F:POPC complex. We propose that discoidal lipid complexes of apoA-I

mimetic peptides are novel platforms for PON1 binding, increasing its stability, and enhancing its activity.

COLL 220

Self-assembling cyclic peptide nanotubes for treating atherosclerosis

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There has been great interest in developing new therapies for atherosclerosis, particularly involving the modulation of high-density lipoproteins (HDL). We report the discovery of self-assembling amphiphilic cyclic peptides that bind and functionally modulate HDLs. The cyclic peptides remodel mature human plasma HDLs into lipid-poor HDLs, which are the initial acceptors of cholesterol in reverse cholesterol transport. Structure-activity relationship studies of the peptides suggest a unique sequence-dependent charge distribution and the requirement for peptide self-assembly processes in the mechanism of action. One of the peptides was found to be active in vivo (mice) in remodeling plasma HDLs for up to eight hours. In a two-week follow-up study involving daily oral administration of the peptide to mice fed a high-fat diet, total plasma cholesterol levels were reduced by greater than 50% compared to controls. Thus, cyclic peptides can serve as a new approach for developing supramolecular agents to treat lipid disorders.

COLL 221

Proteins on the edge (of the lipid bilayer); the structure of NOGO

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Myelin growth inhibitors and their common receptor have been identified as targets in the treatment of spinal cord injury and stroke. We have determined the NMR structure of one of the myelin growth inhibitors, the neurite outgrowth inhibitor (Nogo). We studied the structure of this protein alone and in the presence of dodecylphosphocholine micelles to mimic the natural cell membrane environment. Using several paramagnetic probes, we have defined portions of the growth inhibitor that are accessible to solvent (and consequently the Nogo receptor). Mutagenesis probed through phage-display confirms that the positions predicted to be extra-cellular are sensitive to receptor binding. More recently, we have found a site for specific lipid binding on Nogo. We calculated the optimal protein-protein interface between our structure of Nogo and the Nogo receptor. With these data we predict that residues (28-58) are available to bind the Nogo receptor which is entirely consistent with functional assays.

COLL 222

Membrane binding and regulation of the PTEN tumor suppressor

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PTEN, the PI3K antagonist in the PI3K/Akt signaling pathway, performs its phosphatase activity on PI(3,4,5)P₃ at the plasma membrane-cytoplasm boundary. We performed neutron reflection studies and show that the enzyme scoots peripherally on the membrane. The PTEN crystal structure fits the neutron-scattering length density (nSLD) distribution well, thereby suggesting a low-resolution structure of the protein-membrane complex. All-atom MD simulations support this model by reproducing the experimental nSLD and revealing detailed structural and dynamical aspects of PTEN membrane binding. Comparison with simulations in solution show differences in the organization of PTEN's unstructured C-terminus, thus suggesting a mechanism for the regulation of PTEN membrane association. They also quantify subtle differences of the structures of the protein in a crystal, in solution and after membrane binding. Together, these results provide a reference structure for a critically important cell signaling enzyme on a fluid membrane.

COLL 223

Interferometric nonlinear vibrational spectroscopy probes of solvent and adsorbate structure on mineral surfaces

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A detailed characterization of organic molecule adsorption on mineral surfaces is a fundamental step towards understanding subsequent reactivity in soils, oceans, and the atmosphere. Mineral surfaces serve to sequester molecules, alter their conformation, and orient them. This orientation not only accounts for their specific interaction with and affinity for the mineral, but also governs which chemical functional groups they present to the environment. At the same time, the role of solvent in determining this structure cannot be underestimated as the bulk-phase solvation shell must adapt to the interfacial environment. Equally important, structured water on the minerals is a key characteristic of the surface molecules encounter early in the adsorption process. Over the last decade, visible-infrared sum-frequency generation (SFG) spectroscopy has garnered

attention as it combines excellent specificity for interfacial adsorbate and water molecules, and offers a high degree of structural sensitivity. While SFG spectra serve as fingerprints for mineral-water-adsorbate interactions, it remains a challenge to quantify the underlying structure owing to the complexity of the spectra. Phase-resolved SFG makes a significant contribution towards overcoming this challenge as structural features are more prominent in the real and imaginary spectral profiles. This talk will outline some of our recent efforts at interferometric SFG spectroscopy of water and organic adsorption at mineral surfaces.

COLL 224

Effects of Anions on Heterogeneous Hydrated Fe(III) Oxides Precipitation on Quartz

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Simultaneous homogeneous and heterogeneous precipitation of hydrated Fe(III) oxides on (102) quartz surface were studied with 10^{-4} M Fe(III) at pH = 3.7, in nitrate, chloride, and sulfate solutions. Small angle X-ray scattering (SAXS)/grazing incidence SAXS, atomic force microscopy, and dynamic light scattering measurements were conducted. In all systems, the sizes of the precipitates on quartz were smaller than those in solution. In the sulfate system, fast growth and aggregation occurred, leading to large particle formation. In nitrate and chloride systems, initially, fast heterogeneous nucleation occurred. Then, nucleation, growth, and aggregation occurred in the nitrate system, whereas Ostwald ripening occurred in the chloride system. In the nitrate system, the total particle volume on quartz surface was 10 times more than that in the chloride system. This study provides new important information of anion effects on the heterogeneous hydrated iron oxide precipitation, which helps understand pollutant transport in the environment.

COLL 225

Fe(II) Interactions with Hematite (α -Fe₂O₃) Prepared by Atomic Layer Deposition

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Iron oxides are a ubiquitous class of compounds that are involved in many biological, geological, and technological processes, and the Fe(III)/Fe(II) redox couple is a fundamental transformation pathway. However, the study of iron oxide surfaces in aqueous solution by powerful spectroscopic techniques has been limited due to 'strong absorber problem'. In this work, atomic layer deposition (ALD) thin films of polycrystalline α -Fe₂O₃ were analyzed using the Eisenthal $\chi^{(3)}$ technique, a variant of

second harmonic generation (SHG) that reports on interfacial potentials. By determining the surface charge densities at multiple pH values, the point of zero charge was found to be 5.5+/-0.3. The interaction of aqueous Fe(II) at pH 4 and in 1 mM NaCl with ALD-prepared hematite was found to be fully reversible, and to lead to about four times more ferrous iron ions sorbed per cm² than on fused silica surfaces under the same conditions. The data are consistent with a recently proposed conceptual model for net Fe(II) uptake or release that is underlain by a dynamic equilibrium between Fe(II) adsorbed onto hematite, electron transfer into favorable surface sites with attendant Fe(III) deposition, and electron conduction to favorable remote sites that release and replenish aqueous Fe(II).

COLL 226

Reduction of U(VI) at biological and mineral surfaces: mechanisms and factors controlling the speciation of U(IV)

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The solubility of uranium, a radionuclide contaminant at many sites, is highly dependent on its valence state and speciation. Transformation of U(VI) to U(IV) under reducing conditions can decrease U solubility due to nanoparticulate uraninite precipitation (UO₂); however, recent evidence suggests that U(IV) often occurs in environmental solids as complexed species, e.g. labile precipitates or surface-adsorbed U(IV) atoms. We will present examples of U(VI) reduction by bacteria (*Geobacter*, *Anaeromyxobacter*), by minerals (magnetite, green rust), and by natural sediments where we identified complexed U(IV) species using synchrotron x-ray spectroscopy (XANES, EXAFS). Detailed studies of U(VI) adsorption to carboxyl-functionalized colloids (surrogates for organic surfaces) and subsequent reduction by Fe(II) oligomers or AH₂DS indicate that the presence of trace phosphate or titanium prevent uraninite formation by inner-sphere complexation to U(IV). We will also show how observed U(IV) speciation suggests differences between gram-positive and gram-negative bacteria in their cell-wall electron transfer mechanisms to U(VI).

COLL 227

Effect of salt and pH on the water/silica interface

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Although many environmental processes depend on solvent interactions at mineral/water interfaces, our fundamental understanding is still evolving. For example, while aqueous ionic strength influences silica surface charge and dissolution, the role of

solvent in these processes is unclear. *In-situ* vibrational Sum-Frequency Generation (vSFG) spectroscopy and dynamics of water/silica interfaces at various pH and ionic strengths reveal that the impact of ions on interfacial water strongly depends on pH. The effect of salt on vSFG is strongest at near neutral pH, correlating with the effect of salt on silica surface charge and dissolution described by the 'surface charge sensitivity' model. vSFG provides experimental evidence for the critical role of interfacial water arrangement on chemical reactivity at the solid-liquid interface.

COLL 228

Investigation of silica-water interfaces using forced dewetting coupled with optical spectroscopies

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Forced dewetting is a strategy for physical isolation of ultrathin regions of the solid-fluid interface that can be probed directly with optical spectroscopies. Under the proper conditions, this approach results in residual thin films whose thicknesses are in the nm regime and are dictated by long range as opposed to hydrodynamic forces. These thin films allow examination of the interfacial region without spectral interference from bulk solution. In this presentation, forced dewetting studies are described in which the thicknesses and interfacial molecular structure of interfacial water layers at model silica-water interfaces are probed as a function of pH using ellipsometry and photoelastic modulation-infrared reflection absorption spectroscopy (PM-IRRAS). The thicknesses of these residual interfacial water layers are pH dependent and vary from 6 nm at pH 1 to 9 nm at pH 5.6. These differences are rationalized on the basis of electrostatic contributions to the long range forces dictating residual film formation from pH-dependent silica surface charges. The PM-IRRAS results indicate that the interfacial water layer is significantly more ordered than bulk solution in solutions of any pH.

COLL 229

***In situ* probe of interfacial energies for CaCO₃ heterogeneously nucleated on environmentally relevant substrates**

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The precipitation of carbonate minerals is widely studied due to its importance in marine and sedimentary environments, industrial processes, and geoengineering (e.g., geologic CO₂ sequestration). However, little is known about the thermodynamic factors

controlling the extent of heterogeneous nucleation at mineral surfaces exposed to the fluids in environmental systems. In this study, we probed CaCO₃ nucleation on pristine quartz (100) surfaces in solution and with nanoscale resolution, by using an *in situ* grazing incidence small angle X-ray scattering technique. By measuring nucleation rates at different solution supersaturations, we could obtain an effective CaCO₃/quartz interfacial free energy value of $\sigma' = 36 \pm 5 \text{ mJ/m}^2$ for heterogeneous nucleation. This observation allows quantitative kinetics analysis, and ultimately will lead to precipitation volume estimates that are readily usable in predicting carbonation in many chemical processes and in improving reactive transport models.

COLL 230

Spectroscopic Studies of Molecular Adsorption and Aggregation at Solid/Liquid Interfaces

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Solutes in solution have a choice. They can either remain solvated in the solvent or they can adsorb to a surface. Should solutes adsorb, they might form a terminal monolayer that inhibits further adsorption, or solutes might continue to accumulate leading to the formation of aggregates and/or multilayers. Using TIR-fluorescence and 2nd order nonlinear optical spectroscopy, we examine how subtle changes in solute structure, solvent identity and substrate composition control molecular adsorption and film formation at solid/liquid interfaces. Both steady state and time-resolved data show that strong, multi-dentate association between solutes and silica substrates promote formation of terminal monolayers, while weaker, sterically-hindered solute-substrate interactions generally lead to multilayer formation. These results can also be affected by the identity of the solvent, with aprotic solvents being more likely to enhance film formation beyond the terminal monolayer limit. In some instances, multilayer growth can create new species having markedly different photophysical properties.

COLL 231

Reactivity of Surface Species on Mixed-Oxides: Structural Dependence of Si Reactivity in Alumosilicates

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The kinetics of water-rock interactions are regulated by the reactivities of mineral surface species. For mixed-oxides such as alumosilicates, the same surface species (e.g., silanol) may present different reactivities due to the variation of neighboring atoms in their solid matrix. In this study, the reactivity differences of Si in feldspars were

characterized in terms of Si release rates. Dissolution experiments were conducted at pH ~1.8 for eight natural feldspar samples, differing in interstitial cation and anorthite content. The degree of Al-Si ordering of the samples were characterized using Fourier transform infrared spectroscopy (FTIR) and synchrotron-based X-ray powder diffraction (HR-XRD) and used to interpret the observed Si reactivity difference. A combination of theoretical analysis and experimental results suggested that the random substitution of Al for Si in T2 sites affected the reactivity of Si more significantly than substitutions in T1 sites.

COLL 232

Optical absorption and photoconductivity in epitaxial α - $\text{Cr}_x\text{Fe}_{2-x}\text{O}_3$ films

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Cr_2O_3 and Fe_2O_3 are both wide-gap insulators with bulk band gaps of 2.2 and 3.3 eV, respectively. $\text{Cr}_x\text{Fe}_{2-x}\text{O}_3$ alloys might be expected to exhibit band gaps that scale monotonically with x between these two end-member values, as occurs with Si-Ge alloys. We show that contrary to this expectation, epitaxial films of $\text{Cr}_x\text{Fe}_{2-x}\text{O}_3$ prepared by molecular beam epitaxy exhibit a direct gap that bows downward to a minimum of ~1.8 eV at $x = 0.5$, as determined by optical absorption spectroscopy. Photoconductivity measurements of the band gap are in progress and thus far agree with the optical absorption data quite well. DFT + U calculations of the optical excitation energies have also been carried out and reproduce the experimental trend rather well, provided the magnetic structures of the alloys are accurately accounted for. Band gap lowering this far into the visible is of significant interest for solar light harvesting and photocatalysis.

COLL 233

Polarity in low dimensions

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Polar surfaces present an electrostatic instability requiring substantial charge density modifications to become stable. Microscopic compensation processes have been extensively studied in the last decades[1]. Recently it has become clear that polarity also concerns nano-objects, but that the relevant electrostatic forces and the response they induce differ from the known ones and the influence of the substrate becomes critical. We will exemplify polarity effects in nano-objects of various dimensionality, size

and shapes: ultra-thin films, two-dimensional nano-ribbons and islands and we will highlight some new features of polarity at the nanoscale [2,3].

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COLL 234

Oxide Surfaces

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Oxide surfaces are an important frontier, with numerous applications in areas ranging from catalysis to oxide electronics. Despite this, our understanding of oxide surfaces is relatively primitive. There is a large body of evidence indicating that many oxide surfaces reconstruct with large unit cells, making elemental metals or semiconductors look simple. Indeed, the simplest perovskite SrTiO₃ has many more reconstructions than silicon. Using techniques based upon careful collection of diffraction data coupled with detailed DFT analyses we have made substantial progress in understanding these surfaces over the last few years. For instance, we used a multi-technique solution for a series of reconstructions on the SrTiO₃ (110) surface as well as a large reconstruction on SrTiO₃ (001). In this presentation I will give an overview of these surfaces, as well as some newer information that shows just how complicated oxide surfaces can be.

COLL 235

Atomic structure and reactivity of ferroelectric surfaces: BaTiO₃ (001)

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Surface interactions of ferroelectric compounds are crucial to applications ranging from information storage to catalysis; however, they are inherently difficult to study at the atomic level. This talk will report the reconstructions of BaTiO₃ (001) surfaces, describe the electronic structure and thermodynamic stability of several representative structures, compare the effects of ferroelectric polarization on chemical reactivity, and show the effect of surface overlayers on the stability of surface steps. These results are based on experimental surface analysis (STM, STS, LEED, AES, TPD, etc) and first principles theory.

COLL 236

Oxide materials at the 2-D limit

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Ultrathin oxide films supported on metal surfaces provide oxide-metal hybrid systems with novel structural, electronic, magnetic and chemical properties. Here I will address oxide nanostructures in the ultimate 2-D limit, that is oxide overlayers with only one unit cell in the thickness dimension. We will investigate transition metal oxide monolayer-type structures that are coupled to group VIII or group Ib noble metal single crystal surfaces. Low-D oxide nanostructures on well-defined metal surfaces can be fabricated with atomic-scale precision and design control using bottom-up directed self-assembly and a surface science methodology. The geometric and electronic structure as well as the magnetic properties of Mn oxide and Co oxide monolayers on flat and vicinal Pd surfaces have been examined. It is shown that interface bonding, strain release and finite size effects play an important role in stabilizing novel structure geometries. A complex nano-scale morphology as a result of the interplay of elastic and electronic effects has been found for Mn oxide nanostripes on stepped Pd surfaces, displaying "magic widths" and a significant restructuring of the Pd substrate surface. For Ni oxide on Ag(100), surface embedded nano-island phases have been observed that are discussed in terms of the balance between kinetic and thermodynamic effects, as revealed by DFT calculations. The discussion will then be extended from binary oxides to ternary oxide systems. I will report on the formation and structure of a novel 2-D Cu-tungstate phase, which has been fabricated using oxide clusters and a 2-D solid state chemical reaction route.

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COLL 237

Ultrathin alumina and zirconia: An STM view

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High-resolution scanning tunneling microscopy (STM) has led to significant progress in understanding the structure and reactivity of oxide surfaces, but is virtually impossible on bulk samples of high-bandgap insulator such as Al_2O_3 and ZrO_2 . This problem is circumvented by studies of ultrathin oxides, which provide sufficient conductivity. The talk will describe a few rules for successful preparation of ultrathin oxides by oxidation of an alloy and examples of STM contributions to understanding the crystallography of these films [1-3]. Growth of metals on ultrathin oxides leads to a variety of structures, from single adatoms via well-ordered almost monodisperse clusters [4] to large almost bulk-like particles and films. Binding of metals to these oxides will be also discussed;

the ZrO₂ surface, though oxygen terminated, strongly binds to metals via its Zr atoms [3].

[1] Kresse et al. (2005), Science 308, 1440

[2] Schmid et al. (2007), Phys. Rev. Lett. 99, 196104

[3] Antlinger et al. (2012), Phys. Rev. B 86, 035451

[4] Buchsbaum et al. (2010), Phys. Rev. B 81, 115420

COLL 238

Growth and characterization of conducting oxide single crystals for surface science and other studies

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In spite of their compositional simplicity, binary conducting oxides such as ZnO, In₂O₃, SnO₂, and VO₂ are, in fact, quite complex materials in terms of their physical, electronic, optical, and chemical properties and behavior. These complex properties are generally sensitive to and usually vary significantly as a function of the stoichiometry, purity, and defect characteristics of the material. This complexity, variability, and property dependence continues to drive widespread research efforts on these materials – e.g., on VO₂ whose metal-insulator transition mechanism is still not well understood. Single-crystal specimens, in particular, are extremely valuable for carrying out investigations whose goal is to shed new light on both the surface and bulk properties of these intriguing and useful conducting oxides. Here we describe techniques for the growth of single crystal specimens of ZnO, In₂O₃, SnO₂, and VO₂ and present corresponding results of various recent studies of their surface chemical, structural, and physical characteristics.

COLL 239

Entropy trend for adsorbed molecules, with applications for analyzing TPD

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We present a new way to determine the standard entropies of adsorbed molecules (S_{ad}^0) from TPD data, prove its accuracy by comparison to entropies directly measured using equilibrium adsorption isotherms on MgO(100), and apply it to published data to extract new entropies for adsorbates on single-crystal oxides. Adsorbate entropies linearly track their entropies in the gas-phase at the same temperature (T) as: $S_{ad}^0(T) = 0.70 S_{gas}^0(T) - 3.29R$, where R is the gas constant. These entropies, which are ~2/3 of that for the gas, are huge compared to most theoretical predictions (e.g. the harmonic approximation commonly employed in combination with DFT estimates of reaction

barriers). This relationship can be used to estimate equilibrium constants and rate constants for reactions where such adsorbates are involved, as we demonstrate with prefactors for desorption. Trends in adsorption energies on oxides, some obtained using this method, will be reviewed.

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COLL 240

Osmotic regulation of cell migration and volume in confined microenvironments

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During migration through tissues, metastatic cancer cells experience varying degrees of physical confinement. We hypothesized that cell volume regulation is especially important for migration in confined microenvironments. In combination with live cell imaging, we used a microfluidic-based chemotactic device with narrow extracellular matrix-coated channels to maintain distinct extracellular osmolarities at the leading and trailing edges of the cell. Upon switching from isotonic to hypotonic medium at the top of the chamber, we observed a rapid reversal of cell migration direction. A similar response was observed in multiple cancer cell lines (AB3 mouse sarcoma, HTB-94 human sarcoma, and MDA-MB-231 breast cancer), though the threshold osmolarity necessary to produce a response varied between cell types. Changes in cell migration velocity were accompanied by a decrease in volume, the kinetics and final value of which were dependent on the polarity of the osmotic shock (top, bottom, or top and bottom of the chamber), osmolarity, and cell type. Importantly, inhibition of actin polymerization, but not myosin II, stalled cell reversal after switching medium to hypotonic at the top of the chamber, even though actin-inhibited cells migrated normally during confined migration in isotonic medium. We also observed that microtubule dynamics drive cell polarity changes, and we expect that ion channels and aquaporins will regulate cell volume changes that occur in these confined spaces upon osmotic shock. To further explain our results, we are also developing a theoretical model that relies on flux of ions and fluid flow into and out of the cell. Together, our results indicate that cancer cell migration in confined microenvironments is sensitive to fluctuations in extracellular osmolarity, and the location of osmotic shock (leading vs. trailing edge of the cell) is critical in directing the cellular response.

COLL 241

Controlled liposome fusion mediated by SNARE protein mimics

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The fusion of lipid membranes is essential for the delivery of chemicals across biological barriers to specific cellular locations. Intracellular membrane fusion is particularly precise, and is critically mediated by SNARE proteins. To allow membrane fusion to be better understood and harnessed we have mimicked this important process with a simple bottom-up model in which synthetic fusogens replicate the essential features of SNARE proteins. In our fusogens, the coiled-coil molecular recognition motif of SNARE proteins is replaced by the coiled-coil E/K peptide complex, which is one ninth the size. The peptides are anchored in liposome membranes via pegylated lipids. Here we discuss how the liposome fusion process is controlled by different parameters within the minimal model. The lipopeptide fusogens form specific coiled coils that dock liposomes together, resulting in the merging of membranes via the stalk intermediate. Unusually for model systems, the lipopeptides can rapidly lead to fusion of entire liposome populations and the liposomes can undergo many rounds of fusion. The rate and extent of fusion and the number of fusion rounds can be manipulated by adjusting the fusogen and liposome concentrations.

COLL 242

Cell traction forces as a predictor of cancer cell invasiveness

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Our previous work has linked ECM rigidity to increased matrix degradation by cytoskeletal structures known as invadopodia. Rigidity is sensed by actomyosin-generated contractile forces that are transmitted to the matrix surface as traction forces. Therefore, we hypothesized that traction forces regulate the invasiveness of carcinoma cells in response to ECM rigidity. In this study, we utilized a combined analysis of modified invadopodia and traction force assays to show that ECM degradation and traction forces, respectively, are linear functions of matrix rigidity for SCC-61 cells. In order to determine if ECM degradation is a direct function of traction forces, we treated cells with calyculin A to increase contractility and were able to predict the amount of matrix degradation based on the level of increased traction forces. These data suggest that mechanosensing of matrix rigidity by the actin cytoskeleton via actomyosin contractility may be an important mechanism by which invasiveness is regulated.

COLL 243

Control of Fusion Activities of HIV GP41 and Ebola Virus Fusion Domains by Membrane Lipids

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HIV gp41 and Ebov GP2 fusion domains play critical roles in membrane fusion during viral cell entry. In order to understand how they promote fusion, we have determined the structures of these FDs and several mutants in different lipid environments and correlated them with their fusion activity. Ultimately these studies are designed to find ways to inhibit viral infectivity. Cholesterol is an important mediator of HIV-mediated fusion [Lai, JMB418:3]. In membranes containing <30% cholesterol, the FD forms an alpha helix, but when cholesterol exceeds 30%, the FD forms beta structure. Interestingly, both forms are fusogenic and the most important parameter that determines fusogenicity is the depth of membrane insertion. The Ebov GP2 FD forms a hydrophobic fist-like loop structure in membranes at fusion pH [Gregory PNAS108:11211]. When two critical hinge residues stabilizing this structure are simultaneously replaced by alanines, the native structure is disrupted and fusion is abrogated.

COLL 244

Optical stretching of lipid vesicles to characterize bilayer membrane mechanics

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Lipid membrane bending is an important biophysical process, and an essential element of phenomena including viral infection and synaptic vesicle fusion. We present a method for measuring the bending energy of lipid bilayer membranes by deforming giant unilamellar lipid vesicles (GUVs) in a dual-beam optical trap. This trap is integrated in a microfluidic channel, allowing for large numbers of vesicles to be analyzed sequentially in a flow-through configuration. In each single-vesicle stress-strain experiment, optical force is increased by ramping laser power by a factor of by a factor of 5 over ~15 seconds. Concurrently, vesicle surface area is measured via video microscopy, allowing for area strain to be directly measured. The resulting relationship yields a bending modulus for the vesicle. Early results show that the addition of cholesterol (up to a concentration of 20 mol%) has a negligible effect on the bending modulus of membranes made from singly unsaturated lipids.

COLL 245

Kinetic measurements provide new insights into the folding mechanism of a fusion peptide and its interaction with membranes

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Membrane fusion is one of the key events in many cellular processes and is often assisted or necessitated by membrane fusion proteins, which often contain a membrane interacting domain or a fusion peptide. While fusion peptides have been the subject of many previous studies, their mechanism of action is still not well understood. Herein, using the influenza hemagglutinin fusion peptide (HAfp) as a model, we show how stopped-flow fluorescence, FRET, and pH-jump techniques and global data analysis can be combined to dissect various molecular events underlying peptide-membrane interactions in general and to specifically provide new insights into the folding mechanism of HAfp.

COLL 246

Facile Fabrication of Sub-10 nm Gold Nanoparticles for Visible-Light Carbon Monoxide Oxidation

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Utilizing intrinsic surface properties to direct and control nanostructure growth on a large-scale surface is fundamentally interesting and holds great technological promise. We have developed a novel “bottom-up” approach to fabricating sub-10 nm Au nanoparticles on a nanostructured Ag surface *via* a chemical solution deposition by using localized surface plasmon resonance (SPR) excitation. The Au nanoparticle sizes are tunable from 3 to 10 nm by easily adjusting the deposition time. Unlike the nanoparticles synthesized through wet chemistry methods, these Au nanoparticles are thermally stable and their surfaces are free of organic ligand protection. Moreover, the fabricated Au nanoparticles show high efficiency for CO oxidation in the presence of visible light.

COLL 247

Highly Spectral Dependent Enhancement of Upconversion Emission with Sputtered Gold Island Films

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We report an five-fold overall enhancement of upconversion emission in NaYF₄:Yb/Er nanocrystals when coupled with gold island films. Spectroscopic studies show that the enhancement factors are highly dependent on the exact spectral positions and excitation power density, with a largest enhancement factor more than 12 observed at selected spectral position, which may be attributed to different upconversion processes involved.

COLL 248

Solar Steam Generation using nanoparticles

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Solar illumination of broadly absorbing metal or carbon nanoparticles dispersed in a liquid produces vapor without the requirement of heating the fluid volume. When particles are dispersed in water at ambient temperature, energy is directed primarily to vaporization of water into steam, with a much smaller fraction resulting in heating of the fluid. Sunlight-illuminated particles can also drive H₂O-ethanol distillation, yielding fractions significantly richer in ethanol content than simple thermal distillation. These phenomena can also enable important compact solar applications such as sterilization of waste and surgical instruments in resource-poor locations.

COLL 249

Structural dependence of SERS at silver nanowires and probing preferential facile charge transfer at single crystal TiO₂ particles

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SERS signals at various structures formed by silver nanowires are investigated using confocal Raman microscopy to understand the effect of the density of interstitials on SERS signal. Spatial and spectral dynamics and heterogeneities in both photoluminescence and SERS are compared. Incident laser polarization angle dependence of the SERS intensity and its spatial distribution were revealed using SERS imaging. SERS enhancement capability of interstitials formed by silver nanostructures can be used to understand interfacial charge transfer dynamics at the surface of single crystal anatase TiO₂ synthesized using the hydrothermal reaction. By combining photoelectrochemistry and SERS, the charge transfer mechanism and the preferred transfer pathway within the crystal can be resolved.

COLL 250

Plasmonic stabilization of emissive films for luminescent applications

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Nanotextured metallic films have been used widely for many years to enhance radiative processes including Raman scattering and fluorescence. Here we consider whether emissive rate enhancement for molecules near metal particles can be used to increase the total amount of luminescence derived from an organic film. Increases in emission could have applications to fluorescent dye, phosphor and organic electroluminescent

technologies. We show that we can extract as much as 100 times more light from films of 8-hydroxyquinolinealuminum (Alq_3) on nanotextured silver integrated over their lifetime. Experimentally, we find that this phenomenon cannot be fully explained by excited state lifetime reduction and we present studies to determine the root cause of the large stabilization.

COLL 251

Two-dimensional plasmonic nanosurface for photovoltaics

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We investigate a two-dimensional corrugated plasmonic nanosurface for efficient light trapping in a photovoltaic cell. The design was chosen to minimize light polarization effects and generate robust optical properties for unpolarized sources. It consists of two, perpendicular gratings in the silver film that intersect to yield cross-shaped nano-elements. A thin, silicon film then covers all of this surface structure. An additional degree of freedom can be introduced into the design by interrupting the grid in both directions. We show that this extra spacing between the array elements can be used to tune the absorption properties of the nanosurface. We demonstrate how this two-dimensional configuration is more efficient than its one-dimensional counterpart in terms of the short circuit photocurrent density. We also briefly discuss possible extensions of this structure design, which can further enhance the solar cell performance.

COLL 252

Photocatalysis, thermodynamics, and polarization curves for a fuel cell comprised of an Ag/AgI photocathode and Pt/C anode

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The slow oxygen reduction reaction at traditional platinum cathodes limits the output power of a fuel cell and the economic viability of fuel cells as an alternative energy source. We report a fuel cell where an economical Ag/AgI photocathode replaces the usual Pt/C. Following photo-initiated electron transfer from the silver to the AgI adsorbate layer electron-hole recombination is frustrated by the band gap in semi-conducting AgI facilitating photocatalysis. The resultant anionic adsorbate layer readily delivers reducing equivalents to oxygen nearly eliminating the overvoltage at the cathode, a large source of power loss in the traditional fuel cell. The equilibrium at the Ag/AgI photocathode shifts to the pH-independent iodine (I_2) reduction reaction under irradiation as evidenced by SERS and open circuit cell potential measurements in line with expectations of a Pourbaix diagram. We compare cell voltage and polarization curves for Ag/AgI photocatalytic cell with those observed for the traditional cell.

COLL 253

Long-term stability of metal magic-number clusters

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Magic-number gold clusters have been studied intensely due to their stability and ease of synthesis. Although silver clusters are less stable, their optical properties and low cost are very attractive. The electronic and geometrical shell closings that are used to explain the anomalous abundances of magic-number clusters do not address the long-term stability and decay of these materials, however. Here we use the relative instability of silver clusters to better understand the nature of metal cluster stability. We studied the stability of a family of silver glutathionate magic-number clusters as function of size, electrostatic and chemical environment. Stability was found to be a non-monotonic function of size, with larger clusters decaying into smaller clusters of previously known sizes. The net surface charge was important for stability while charge screening was not, in contrast to DLVO theory. Using these results, new methods for synthesizing specific cluster sizes could be found.

COLL 254

Overcoming kinetic barriers to self-assembly using directing fields

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The rapidly expanding library of nanoparticles with complex shapes and chemistries provides new opportunities to create functional self-assembled materials from these building blocks. However, kinetic arrest often frustrates the formation of the equilibrium phase encoded by the colloidal interactions or particle shape. Directing fields have proven effective at circumventing kinetic arrest. In this work, we demonstrate that, by aligning anisotropic dumbbell particles in a steady ac electric field during convective deposition, their glassy arrest in a disordered structure can be avoided, leading to close-packed crystals [1]. In a second example, we toggle an external field at varied frequencies, causing field-induced gel-like structures in a magnetorheological (MR) fluid to relax periodically to equilibrium [2]. This demonstrates how kinetic barriers to a colloidal phase transition are also subverted through measured, periodic variation of driving forces.

[1] Forster, J. D. et al. Assembly of optical-scale dumbbells into dense photonic crystals. *ACS Nano* 2011, 8, 6695–6700.

[2] Swan, J. W. et al. Multi-scale kinetics of a field-directed colloidal phase transition, *Proc. Natl. Acad. Sci. USA* 2012, 109, 16023-16028.

COLL 255

Magnetically Directed Assembly and Dynamic Manipulation of Binary Colloidal Crystals

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Assembly of microscopic particles into macroscopic structures can open new pathways for the fabrication of complex materials and devices that cannot be produced via lithographic methods. Here we demonstrate a versatile colloidal assembly system in which the design rules can be tuned to yield over 20 different pre-programmed structures, including kagome, honeycomb, square tiles, as well as various chain and ring configurations. These structures can be dynamically tuned with the external field. The assemblies are created by controlling the relative concentrations and interaction strengths between spherical magnetic and non-magnetic beads, which behave as either paramagnetic or diamagnetic dipoles when immersed in a ferrofluid. An external magnetic field causes like particles to repel and unlike particles to attract. The combination of experimental observations and potential energy calculations suggest that the lowest energy configuration is determined by two parameters, namely the relative strengths of the two dipole moments and their relative concentrations.

COLL 256

Dipolar assembly and colloidal polymerization of magnetic nanoparticles and nanorods

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Ferromagnetic colloids based on metallic cobalt are an interesting class of nanoparticles capable of self-assembly via spin dipolar interactions. We will present an overview of our efforts on the synthesis, functionalization and assembly of polymer coated ferromagnetic cobalt nanoparticles. A novel synthetic methodology, termed, "Colloidal Polymerization" will also be discussed where ferromagnetic polystyrene coated cobalt nanoparticles were used as "colloidal monomers" to form fused cobalt oxide nanowires. Using a combination of dipolar assembly and a nanoparticle conversion chemistry (e.g., oxidation, galvanic exchange), cobalt oxide nanowires with controlled placement of noble metal and semiconductor inclusions has been achieved. We will discuss our recent efforts to control the sequence, composition and architecture of these dipolar

assemblies and the resulting electrochemical properties of the converted cobalt oxide nanocomposites.

COLL 257

Modeling of experimentally studied charged nanoparticle at electrified liquid/liquid interface

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Voltage control of the surface of charged nanoparticles influences the order of their interfacial assembly, which can lead to different optical, magnetic, and electrical functionality. X-ray reflectivity and GISAXS measurements demonstrate that cationic gold nanoparticles penetrate further into the 1,2-dichloroethane (DCE) side of an electrified water/DCE interface as the applied voltage is increased. A similar trend is also observed in molecular dynamics (MD) simulations of a single nanoparticle at the interface. Ion-ion and ion-nanoparticle correlations and their distributions are studied using an atomistic model. We found that there is a strong correlation between the charged nanoparticle and supporting electrolytes in the DCE phase. Results from different simulation systems will be compared to address the effect of the field, counterions, and electrolyte concentration. These studies address the question of which interactions determine the interfacial localization of charged nanoparticles. Future work will include MD simulations to illustrate the self-assembly of multiple charged nanoparticles that has been observed in experiments.

COLL 258

Locking nanoparticles

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We report an approach to surface modification of nanoparticles with responsive mixed polymer brushes. It was demonstrated that the nanoparticles are capable of reorganization in an external magnetic field, which can turn on interactions between the particles. The interaction remains unchanged even after removal of the external magnetic field. The “locking particles” can be unlocked by applying external stimuli. In essence, we have shown that the balancing Brownian motion, the short-range attractive

and long-range repulsive forces due to the specially tailored mixed polymer brush shell of the particles, and the forces experienced by the particles in the external field constitute a method to fabricate and reversibly lock 1D wires/chains in liquid matrixes (solvent or polymer melt). We also demonstrated that a mixture of two populations of nanoparticles with different surface functionalization that provide control over intermolecular forces can be used to regulate the length of self-assembled 1D wires.

COLL 259

Printing, probing, and analyzing nanoliter droplets with magnetic nanorods

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Magnetic nanorods are attractive materials enabling assembly, ordering, control, and reconfiguration of different magnetic lattices within milliseconds. MilliTesla magnetic fields are sufficient to manipulate with these nanorods. In this talk, a few examples of applications of magnetic nanorods will be shown. First we will discuss the remote controlled rotation of magnetic nanorods providing a new nanoscale tool to probe different properties of liquids and solids at the micrometer scale. In particular, we will show that with magnetic nanorods one can address the current challenge of the in situ characterization of minute amounts of fluids rapidly changing their rheological properties. Basic theory of Magnetic Rotational Spectroscopy for rotation of a magnetic nanorod in non-Newtonian fluids will be introduced and specific features of rotating nanorods will be explained. Then we will experimentally demonstrate that magnetic rotational spectroscopy provides rich physicochemical information about the gelation processes of polymers and sols. We will show that one can analyze not only polymer solutions, but also suspensions enriched with the gel domains being formed. Then we will demonstrate a new physical principle of self-assembly of magnetic nanorods into droplets of different sizes without using any nozzle. These droplets can be formed on demand by taking advantage of the magneto-static interactions between nanorods. Using X-ray phase contrast imaging and scaling analysis we will explain the behavior of magnetic nematics and their interactions with the droplet surface.

COLL 260

Multiplexed motion of magnetic beads on a magnetic ratchet

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Thermally or deterministically-driven transport of objects through asymmetric potential energy landscapes (ratchet-based motion) is of considerable interest as models for

biological transport and as methods for controlling the flow of information, material, and energy. Here, we provide a general framework for implementing the multiplexed separation of magnetic colloids based on size. Our approach is based on quasi-static (adiabatic) transitions in a tunable potential energy landscape composed of a multi-frequency magnetic field input signal with the static field of a spatially periodic magnetization. By tuning both the phase shifts between the input signals and the relative forcing coefficients, medium sized particles can transport across the substrate, whereas large or small-sized particles remain trapped in closed orbits (i.e., a bandpass filter). The reverse situation in which large and small size particles can be transported, whereas medium sized particles are trapped in closed orbits, can also be achieved (i.e., a bandgap filter).

COLL 261

Magneto-Acoustic assembly of binary colloidal lattices

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Self-assembly of colloidal particle suspensions into a variety of lattice structures has potential applications in photonics and biomedical sciences. Among the many different colloidal assembly techniques, field assisted assembly has the potential to create tunable interactions, which can guide particles into various crystalline configurations. In this work, we combine acoustic field and magnetic field to simultaneously control the assembled structures at both micro and macro scale. The acoustic field allows the particles to be concentrated into well defined regions of pressure minima at the macro-scale. The magnetic field allows the micro-scale to be controlled by tuning the interactions between paramagnetic and non-magnetic particles in ferrofluid solution. In some cases, the competition between the acoustic and assembly fields led to the creation of several unique novel non-planar structures. The ability to control local particle concentration, in particular, has the analogous effect of realizing different colloidal pressures, which may serve as a useful tool in bridging the gap between simulation and experiment.

COLL 262

High-rate Electro-fluidic Directed Assembly of Nanoparticles

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Directed assembly of nanoelements has been used to fabricate devices for diverse applications. The challenge in using such techniques consists of developing highly scalable, high-rate (fast) assembly techniques for placing nanoelements precisely on either conductive or insulating surfaces. Here, we introduce a new, high-rate electro-fluidic assembly technique that enables directed assembly on any type of insulating surfaces. The significance of this technique is that the assembly process is 100 times faster than fluidic assembly (the only technique used today on insulating surfaces). For example, fluidic assembly on a 3-inch wafer takes 25 hours; however, the presented method takes only 15 minutes to obtain fully assembled structures. Polystyrene Latex nanoparticles (50nm and 20nm) have been successfully assembled. We are able to achieve full particle coverage with trenches having different orientations and structures that exhibits the robustness of the assembly method for any two dimensional configuration.

COLL 263

Single Nanoparticle Plasmonics

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Interest in nanotechnology is driven by the unique and novel properties of nanoscale materials such as the strong interaction of metal particles with light, caused by localized surface plasmon resonances (LSPRs). This effect can be by utilized in sensors and optical devices, for which the characterization, control, and optimization of the shape- and size-dependent optical properties is paramount. Our studies took advantage of the well-defined shape and large size range of the Ag nanocubes provided by Younan Xia's group. Single nanoparticle correlated LSPR/electron microscopy/electrodynamics calculations quantified differences between otherwise identical Au and Ag cubes, while detailing the size-dependence of their resonance energy and substrate effects. Further correlation with polarization-dependent scanning photoionization microscopy shows strong electric field enhancement of the laser-induced photoemission, identifying coherent multiphoton photoelectron emission (MPPE) as the most probable mechanism for electron emission from Ag nanocubes.

COLL 264

Plasmonic enhancement of light scattering in cellular and molecular imaging reveals the secrets of cancer cells in life and in death

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Using the Plasmonic enhancement of Rayleigh scattering by silver or gold nanoparticles, we were able to image the behavior of community of cancer cells as they are dividing or dying if we increase the concentration of the nanoparticles at the cell nucleus. In order to gain molecular information, we were recently able to record the enhanced molecular Raman vibration spectra (SERS) of the molecules anywhere in the cell during the full cell cycle from birth to division(1) or if we give the cells cancer drugs, we can determine the time of the cell death. The potential future applications of this technique of PLASMONIC ENHANCED MOLECULAR CELL IMAGING (PEMCI) in molecular cell biology and in medicine will be discussed.

1. Bin Kang , Lauren A. Austin , and Mostafa A. El-Sayed, Real-Time Molecular Imaging throughout the Entire Cell Cycle by Targeted Plasmonic-Enhanced Rayleigh/Raman Spectroscopy, , *Nano Lett.*, 2012, 12 (10), pp 5369–5375.

COLL 265

Gold nanorods: their ins and outs

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Anisotropic noble metal nanostructures, such as gold nanorods, can be prepared in aqueous solution with good control over nanoparticle dimensions. In this talk I will summarize some of our recent results in understanding gold nanorod growth, the nature of the surface under various conditions, and what new properties are enabled for nanoscale plasmonic particles.

COLL 266

Directing the morphology and assembly of gold nanoparticles

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The assembly of nanoparticle building blocks is a pre-requisite for the amplification of the properties of the components and/or the generation of new features unique to the ensemble. Usually, nanoparticles employed for these assemblies are spherical and lack a geometrical preference toward directional self-assembly, thus limiting their potential applications. In contrast, controlled self-assembly of non-spherical nanoparticles, such as gold nanorods, enables these arrays to form defined 1D, 2D or 3D structures with a vectorial dependence of the desired properties. We show in this communication several examples where the morphology of gold nanoparticles can be modulated by means of

colloid chemistry methods, and in turn exploited to direct the assembly of such nanoparticles into a variety of nanostructures with interesting properties.

COLL 267

Controlling the Shape of Silver and Gold Nanostructures with Reaction Kinetics and Surface Chemistry

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We have shown that we can control the growth of silver and gold nanoparticles from small, spherical seeds into anisotropic structures with well-defined shapes and sizes. We have achieved this control over particle morphology by developing an understanding of the underlying chemistry. A major factor which directs a particle's growth pathway is reaction kinetics, which can be controlled by varying reducing agent concentration, solution pH, and the presence of halides, which change the reduction rate of the precursor metal ions. In the plasmon-mediated synthesis of silver nanoparticles, reaction kinetics also can be adjusted by taking advantage of the localized surface plasmon resonance properties of the particles and tailoring the properties of the light used to irradiate the plasmonic seed particles. Surface chemistry also influences growth, exemplified by the passivation of select surfaces of gold nanoparticles by silver. The synthesis of novel nanomaterials using these synthetic routes will be discussed.

COLL 268

Silica and Cells: A special relationship

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We have shown that yeast, bacterial, and mammalian cells, when introduced into self-assembling solutions of phospholipids and soluble silica, serve as *living colloids* directing the formation of unique cell/silica interfaces (*Science* 2006, *Nature Chem Biol.* 2010) and architectures through cellular response pathways. The association of silica with cellular interfaces has been further explored in recent work, where we have discovered a process, *Silica Cell Replication* (*PNAS* 2012), wherein mammalian cells direct their exact replication *in silica*. The silica cell replicas preserve nm- to macro-scale cellular features and dimensions on both the cell surface and interior after drying at room temperature - and largely after calcination to 500 °C. The process appears to be self-limiting and self-healing, and remarkably generalizable to any cells of interest. Our current hypothesis is that, due to comparable hydrogen bonding strengths, silicic acid molecules replace bound water at cellular interfaces and are amphotERICALLY catalyzed

by proximal proteins and other membrane bound components to form a self-limiting, defect-free, nm-thick silica encasement that resists drying and calcination stress.

COLL 269

Interactions of peptides and ions with supported lipid bilayers

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Lipid membranes often contain negatively charged lipids such as phosphatidylserine, phosphatidylglycerol, phosphatidic acid, and gangliosides. The head groups of these lipids contain carboxylate and phosphate groups which can interact with cations and positively charged amino acids. Moreover, such lipids are often heavily regulated within cells and appear in much greater abundance in the membranes of particular organelles and even specific leaflets within these membranes. We have used a combination of spectroscopic techniques, microfluidic platforms, and planar supported bilayer architectures to study the chemical specificity of positively charged analytes with these moieties. Both thermodynamic data and the molecular level details of the systems are obtained. The results reveal that binding can not only be highly dependent on the specific chemistry of the ligand-receptor interactions, but also on the concentration of negatively charged lipids, the presence of additional uncharged lipids in the membrane and the chemical nature of the positively charged groups which are binding. In fact, the specific chemistry of these interactions (hydrogen bonding, charge transfer, hydrophobic interactions, etc...) often dominates over generic electrostatic effects.

COLL 270

Interaction of complex liquids with lipid biomembranes

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With the increasing use of smart molecular probes and functional nanocolloids for various biomedical applications, it becomes critical to understand the interaction of complex liquids with cell biomembranes in order to effectively use them with minimal cytotoxicity. Deciphered by fluorescence imaging and fluorescence correlation spectroscopy in combined with other traditional characterization, this talk will emphasize some recent studies in my group of how ionic liquids, nanocluster macroions, and nanoparticles interact with cell biomembrane. Using lipid bilayers as model biomembranes, I will show that adsorbed molecules and nanocolloids can not only disrupt the morphology of lipid bilayers, but also induce their phase transition due to sufficiently strong electrostatic attraction. With ionic liquids and nanocluster macroions whose dimensions are comparable to lipids, intriguing supramolecular assembly is also observed at lipid bilayer interface, showing a strong dependence on the chemical makeup of adsorbed ionic species.

COLL 271

Synthetic colloidal particles cloaked by natural RBC membranes as biomimetic delivery vehicles

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Efforts to extend nanoparticle residence time in vivo have inspired many strategies in particle surface modifications to bypass macrophage uptake and systemic clearance. Herein I report a top-down biomimetic approach in particle functionalization by coating biocompatible nanoparticles with natural red blood cell (RBC) membranes including both membrane lipids and associated membrane proteins for long-circulating cargo delivery. This approach aims to camouflage the nanoparticle surface with the erythrocyte exterior for long circulation while retaining the applicability of the cores that support the RBC membrane shell. In vivo results revealed superior pharmacokinetics and biodistribution by the RBC-mimicking nanoparticles as compared to control particles coated with the state-of-the-art synthetic stealth materials.

COLL 272

Layering polymers and nanoparticles at surfaces: Towards spatially organized, responsive assemblies

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We discuss principles of construction of layered, responsive, all-polymer or polymer nanocomposite materials using a layer-by-layer (LbL) approach. With all-polymer films assembled electrostatically, we first explore polymer chain dynamics and its relationship to film structure. A combination of fluorescence recovery after photobleaching (FRAP) and neutron reflectometry (NR) to probe chain diffusion in directions parallel and perpendicular to the substrate, respectively, reveals that at increased salt concentration, polyelectrolyte chains move orders of magnitude faster in the direction parallel to the substrate. Solution pH, salt concentration and polyelectrolyte type strongly affect mobility of polyelectrolyte chains within LbL films and the degree of film layering. We then introduce assembly of responsive, layered nanoparticle-polymer films. Such materials demonstrate light-triggered, strata-specific shrinkage at resonant excitation wavelengths, enabled by precise localization of brush-decorated gold nanostructures within LbL films. We discuss potential applications and future development of responsive polymer-nanoparticle LbL assemblies.

COLL 273

Organization and Dynamics of Cell Signaling in the Immunological Synapse

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A major challenge in biological science and engineering is to understand and control how cells communicate. When cells transduce signals, thousands of membrane receptors and signaling molecules reorganize into spatially diverse patterns over many length scales. Such dynamic process is a key element to ensure the spatiotemporal connectivity in cellular signal transduction. A hallmark example is the tight membrane junction between immune cells, namely the immunological synapse. Membrane receptors reorganize to form protein patterns on multiple length scales from nanometers to micrometers. It has been recognized that the spatial organization of proteins is directly associated with immune responses, but the underlying mechanisms remain unclear. In the presentation, I will describe how advanced fluorescence imaging, nanotechnology, and cell biology can be combined to understand the protein organization and dynamics in the T cell immunological synapse during signal transduction. A combination of multidisciplinary approaches, including single-molecule imaging and tracking, lipid bilayer engineering, and surface fabrication, allow us to elucidate the interconnectivity between physical phenomena and biochemical signaling.

COLL 274

Efficacy of broad spectrum antimicrobials within heavy traffic textured surfaces

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With the increase in antibiotic-resistant microbes, the production of self-decontaminating surfaces has become an area of research that has seen a surge of interest in recent years. Such surfaces, when incorporated into commercial products such as children's toys, medical devices and hospital surfaces could reduce the number of infections caused by pathogenic microorganisms. Within many commercial applications the use of textured non-slip surfaces are frequently utilized in order to increase traction and reduce the risk of injury; however, frequently these rough surfaces are the cause of abrasions in the event of a fall. Research in our laboratory has recently focused on the development of a wide range of amphiphilic antimicrobial additives that when combined with low volatile organic content coatings afford surface concentration of the active compounds as the coating cures. We report the development of antimicrobial coatings containing a variety of additives that are active against a broad-spectrum of potentially pathogenic bacteria, as well as enveloped viruses and fungi. Additionally, these additives were compatible with siloxane, urethane and acrylate coatings which have a broad range of real world situations. The efficacy of these surfaces with exposure to environmental conditions and wear will be presented along with detailed surface characterization.

COLL 275

Plasmonic–Magnetic Nanoparticles for Diagnostics, Isolation, and Photothermal Destruction of Biomolecules

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We discuss the development of a plasmonic–magnetic nanotechnology-driven approach for the targeted diagnosis, isolation, and photothermal destruction of biomolecules. Experimental data show that aptamer-conjugated plasmonic/magnetic nanoparticles can be used for targeted imaging and magnetic separation of a particular kind of biomolecules from a mixture. We also discussed that the *aptamer-conjugated* magnetic/plasmonic nanoparticle-based photothermal destruction of biomolecules is highly selective.

COLL 276

Biocompatible Multifunctional Nanoparticle for Multimodal Imaging & Therapy of Methicillin-resistant Staphylococcus aureus

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Last few years a complex problems facing our society is treating *Methicillin-resistant Staphylococcus aureus* (MRSA) infectious. Here we will discuss the development of multifunctional nanoparticle for multimodal imaging and therapy of MRSA infections. We will discuss the possible mechanism and operating principle of multimodal imaging and therapy process.

COLL 277

Hybrid CNT/Gold Nanomaterial for Targeted Imaging and Photothermal Destruction of Biomolecules

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Here we discuss **the design of novel aptamer conjugated different shape gold nanoparticle decorated SWCNTs hybrid nanomaterial for targeted imaging and selective photothermal destruction of biomolecules. We will discuss the possible mechanism and operating principle for our process.**

COLL 278

NMR Analysis of Polymeric Alpha-nucleophiles as Potential Chemical Weapon Decontamination Agents

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NMR Analysis has been used to examine the ability of polymeric alpha-nucleophiles containing oxime or oximate functional groups to decontaminate super-toxic materials, including VX and sulfur mustard(HD). Chemical cascades are presented that can be triggered by synthesis of peracids on demand. Polymeric alpha-nucleophiles such as polyacrylamidoxime (PANOX) and poly(N-hydroxyacrylamide) (PHA) are potent hydrolysis agents of chemical warfare agents (CWA) such as S-2-(diisopropylamino)ethyl O-ethyl methylphosphonothioate (VX), especially when converted to their respective oximate salts at pH values greater than the pKa of oximate or amidoximate groups of 7.5 and 10.8, respectively. In the present work, we arrived at formulations that possess a universal capability of destroying CWA. By electrostatic complexation of polyanionic sodium salts of PANOX and PHA with cationic bleach activator, N-[4-(triethylammoniummethyl)benzoyl] butyrolactam chloride (TBBC), we obtained complexes that generate peracids in situ in the presence of alkaline hydrogen peroxide or ozone. The latter are generated electrochemically on demand, thus triggering peracid formation and facile degradation of HD. Organophosphorous esters such as VX are hydrolyzed by the action of nucleophiles in the presence of water. Results of the CWA degradation by MAS-NMR and other analytical techniques are presented.

COLL 279

Admicellar Polymerization to compatibilize calcium carbonate with oil-based drilling mud: To improve mud performance

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Surface modification of industrial grade extra-fine calcium carbonate (XFCC) via admicellar polymerization has been examined as a method to enhance compatibility of the substrate with oil-based drilling mud (OBM). A thin film of polystyrene was synthesized within the admicelles of Triton X-100 surfactant using 2,2'-azobisisobutyronitrile (AIBN) as the initiator. The extracted polymer from the treated substrate was analyzed and characterized using FTIR, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The process presents a possible inexpensive technique to modify calcium carbonate's high energy hydrophilic surface into a low energy hydrophobic surface. The modified

substrate, used as densifier in OBM, is expected to be more compatible with the OBM, enhance homogeneity, improve drill cuttings removal and increase fluid reuse.

COLL 280

P(VI) and p(4-VP) polymeric particles and their silica composites for situ Co and Ni nanoparticles and their use as catalyst in NaBH₄ hydrolysis

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Poly(vinyl imidazole) (p(VI)) and poly(4-vinylpyridine) (p(4-VP)) particles and their composite with silica as (p(VI)-Si) and (p(4-VP)-Si) were synthesized in an oil-in-water micro emulsion system. Pores were generated inside particles by removing silica from p(VI) and p(4-VP) composites upon HF treatment. The sizes of particles were ranged 300-800, and 300-600 nm for p(VI), and p(4-VP), respectively. Co and Ni metal nanoparticles were prepared within p(VI) and p(4-VP) based particles by the absorption of the corresponding metal ions from aqueous solution and reduction with NaBH₄ in situ. Different parameters affecting the hydrogen production rate from the hydrolysis of NaBH₄ such as metal types, temperature, NaOH concentration, and metal reloading were investigated. For the p(VI)-based particles, the activation energy, the enthalpy, and the entropy for the NaBH₄ hydrolysis reaction were also calculated as 37.578 kJmol⁻¹, 34.146 kJmol⁻¹, and -191.22 kJmol⁻¹K⁻¹, respectively.

COLL 281

P(4-VP) particles with high functional value

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Poly(4-vinyl pyridine) (p(4-VP)) particles were synthesized using ethylene glycol dimethacrylate (EGDMA) as cross-linker and ammonium persulfate (APS) as initiator in a microemulsion system. The synthesized p(4-VP) particles were modified with various modifying agents. The modification was carried out using N-alkyl quaternization agents such as 2-bromo ethanol (-OH), 4-bromo butyric acid (-CO₂H), 4-bromo butyronitrile (-CN) and 2-bromoethylamine hydrobromide (-NH₂). The size and charge characterization of particles were done using DLS and Zeta potential measurements, and the modification is confirmed by FT-IR spectrophotometer and titrations. SEM and/or optical microscopy were used for the visualization of particles. The modified p(4-VP) particles were tested for antimicrobial properties against various bacteria such as *Staphylococcus aureus* ATCC 25323, *Escherichia coli* ATCC 8739, *Bacillus subtilis*

ATCC 6633. And the absorption of various species such as metal ions (Co, Ni etc), dyes (Rhodamine 6G, fluorescein sodium salt) and pesticide (paraquat) onto p(4-VP) based particles were also investigated.

COLL 282

Analysis of surface segregating additives for self-decontaminating coatings

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Surface contamination resulting from a toxic chemical release poses significant risk to first responders as well as proximate civilians. Recent progress in self-decontaminating coatings has demonstrated the potential for coating surfaces to automatically degrade harmful chemicals upon contact. Herein, reactive additives developed to impart self-decontaminating capability to polyurethane polymer matrices are discussed. Specifically, synthetic modification of fullerene and polyoxometalate based additives resulted in surface segregating molecules which effectively reduced required additive loading concentration while maintaining desired decontamination ability. Hydrophobic and hydrophilic moieties were incorporated into both additive classes resulting in a series of molecules exhibiting a range of amphiphilic character. Effects on surface properties from additive incorporation into commercial polyurethane coatings were investigated by SEM, EDS, ATR, contact angle, and confocal laser microscopy. Surface segregating capabilities were analyzed and loading concentrations were optimized for maximum contaminant degradation. Furthermore, potential degradation pathways deduced from contaminant challenge by-product analyses are discussed.

COLL 283

Humic Acid particles: Synthesis and Characterization

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Humic acid (HA) is very important natural material in soil fertility, transport of pollutants, sediments, and in natural waters due to the different functional groups which are capable of binding to metal ions, mineral surfaces and organic contaminants. Due to the phenolic and carboxylic acid groups in the natural humic acid substances, the surface charge and the reactivity of HA is mainly variable depending on the medium and the nature of HA. In this investigation, novel humic acid hydrogel particles were prepared in a single step via a water-in-oil microemulsion system employing different crosslinkers as

divinylsulfone, glutaraldehyde, epichlorohydrine, and adipoyl chloride. Scanning electron microscopy (SEM), dynamic light scattering (DLS), zeta potential measurement were used for the characterization of humic acid particles size, charge, and morphology. Thermal and structural properties of the crosslinked humic acid particles were evaluated by thermogravimetric analysis (TGA) and FT-IR spectroscopy.

COLL 284

Self-assembly of poly(4-vinyl-N-alkylpyridinium) bromide onto silica: Effect of side-chain length on structural aspects at a molecular level

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Self-assembly of poly(4-vinyl-N-alkyl)pyridinium bromide with alkyl side chains of 2, 5, 7, 10 or 16 carbons from ethanolic solutions onto flat silica surfaces was studied by means of ellipsometry, atomic force microscopy (AFM), contact angle measurements and Sum-Frequency Generation vibrational spectroscopy (SFG) in the CH₃ and CH₂ stretch region. SFG results showed that longer side chains promote the disorientation of the alkyl groups at the surface, corroborating with the contact angle values. *Ab initio* quantum-chemical calculations on the N-alkylpyridinium side-group with Restricted Hartree-Fock (RHF) method and 6-311G (d,p) basis set were done to estimate the charge distribution along the pyridinium ring and the alkyl side-chain. Quantum-chemical optimization and Mulliken electron population showed that from C2 to C15 the positive charge at the head group (HG) decreased 0.025, while the charge at combined HG + α -CH₂ increased 0.037 and for C6 or longer, the alkyl side group presents a tilt in the geometry, moving away from the plane.

COLL 285

Selective Detection and Photothermal Therapy of Cancer Cells using Iron Core Gold Shell Nanoparticles: SWCNT Hybrid Nanostructures

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Due to the fact that gold nanoparticles possess unique optical properties and are considered to have low toxicity toward humans, the use of gold nanoparticle based biological detection devices and therapeutic agents are very attractive. Multifunctional nanomaterials can potentially be even more superior because more than one physical property can be exploited to target or separate a particular biological agent. Single walled carbon nanotubes (SWCNTs) arrayed with iron core gold shell nanoparticles

have the potential to be used for medical diagnosis via MRI because of the magnetic properties of the iron core, and the plasmonic gold shell can be useful for photothermal therapy through irradiation at a specific wavelength or cancer detection through surface enhanced Raman spectroscopy. After synthesizing the desired iron oxide nanoparticle, a specific synthetic protocol was used to encase the iron nanoparticle with a gold nanoparticle thereby creating a gold nanoshell. Confirmation of the encapsulation of the iron nanoparticles with gold nanoparticles was realized through a combination of UV, Raman spectroscopy, and TEM. These iron core gold shell nanoparticles were then anchored onto a functionalized SWCNT through the formation of a sulfur carbon bond. TEM images provided evidence of the gold shell/iron core nanoparticle decorated SWCNTs.

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COLL 286

Directed Assembly of Porphyrins and Phthalocyanines on Graphitic Surfaces

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One application of graphene, a two dimensional allotrope of carbon, is its use as the semiconducting channel in field-effect transistors (FETs). Since the conductivity of the channel is dependent on the transport properties of the material, shifting the bandgap of graphene through n- or p-type doping can fine tune the FET switch point. To achieve this, the directed assembly of porphyrinoids through the oxidation of highly ordered pyrolytic graphite was studied. Oxidation was achieved locally through atomic force microscopy (AFM) biased lithography and on a larger scale through UV-Ozone. The resulting porphyrinoid on graphite oxide was then studied with Raman spectroscopy and AFM for identification and coverage calculations. Once the different interactions are understood for the complete set of porphyrinoids the system can be applied to graphene. Then with appropriate combinations of electron donating and withdrawing porphyrinoids highly tailored FETs can be developed.

COLL 287

Stable Anisotropic Gold Nanoparticles and Their Applications as Photothermal Heating Materials

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A simple synthetic method is proposed to prepare stable anisotropic gold nanoparticles possessing a strong and broad absorption band in the presence of poly(*N*-isopropylacrylamide). The resulting nanoparticles were thoroughly characterized by UV-visible spectrophotometer, scanning and transmission electron microscopes, and dynamic light scattering, infrared spectrometer, Raman spectroscopy, and gel permeation chromatography. These anisotropic gold nanoparticles exhibited prolonged stability and showed efficient photothermal heating of water upon exposure to solar-simulated light due to the unique optical property and high surface-to-volume ratio. Subsequently, these nanoparticles were employed in the carbon-carbon bond forming reaction in the presence and absence of light irradiation to examine their catalytic efficiency. The reaction rate and yield was generated enhanced in the presence of these anisotropic gold nanoparticles under light irradiation.

COLL 288

Peracid-modified silica as heterogeneous oxygen transfer agents

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Alkyl and aryl peracids have been incorporated onto silica materials either by sol-gel synthesis or by grafting of nitrile or ester groups, which were subsequently hydrolyzed and oxidized. These materials have been characterized by FTIR, TGA, solid-state NMR, and iodometric determination of peracid content. The peracid-modified silicas were evaluated as oxygen transfer agents for the epoxidation of linear and cyclic alkenes (e.g. *n*-octene, cyclohexene, cyclooctene and styrene). The use of sol-gel materials resulted in better selectivity towards epoxide formation compared to grafted materials. The higher surface density of silanols in the latter may have contributed to the ring-opening of the epoxides into the diols. We can tune the selectivity and throughput of our heterogeneous oxidants by varying key parameters such as the structure and surface density of the peracids, as well as the structure and surface density of silanol-capping moieties. In addition, these organic-inorganic hybrid materials are advantageous for ease of handling and separation of products, can be regenerated, and can be readily adapted for either batch or flow systems.

COLL 289

Giving polypeptide colloidal hybrid particles a gentle buzzcut

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This work explores the capability of the NaOH etching process for controlling the morphology of SiO₂ particles coated by a homopolypeptide shell. Polypeptides such as poly (*N*^ε-carbobenzyloxy-L-lysine), PCBL and poly (*o*-benzyl-L-tyrosine), PBTYR, were

grown by ring opening polymerization of the corresponding *N*-carboxyanhydrides initiated by amino functional groups, decorating the silica surface. These hybrid particles, either covalently doped with fluorescein isothiocyanate, FITC, or lacking it, have shown different mesoporous structures upon treatment with solution of NaOH as a consequence of the selective etching from the interior. The polypeptide shell seemed to stabilize the surface against chemical etching. A key approach was developed to assess the molecular weight of the grafted polymers on silica surface. Comparative control experiments conducted on untethered polypeptide have demonstrated that polypeptide degradation did not occur during the treatment and did not affect the value of the molecular weight.

COLL 290

Self-assembly of Amyloid Beta Peptide over Nitro-Dialkoxy Disulfide Functionalized Nano Gold Colloidal Particles

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Aiming to more stably produce an oligomer form of amyloid beta (i.e., a key intermediate of fibrillogenesis which eventually leads to Alzheimer's disease), the surface of gold colloids were functionalized with nitro-dibenzyloxy disulfide. The reversible color change was observed over for all sizes of the tested gold colloidal particles ranging between 10 nm and 100 nm. Functionalization of gold colloidal surface with nitro-dibenzyloxy disulfide achieved larger amplitude in repetitive peak shift between pH 4 and 10 implying a formation of an oligomer under the reversible process.

COLL 291

Application of 1,3-Dipolar Cycloaddition toward SWCNT Functionalization and Subsequent Attachment of Gold Nanoparticles

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Similar to other allotropes of carbon, single walled carbon nanotubes (SWCNTs) are insoluble in a variety of solvents. A number of synthetic methods have been used to add non-carbon functional groups to SWCNTs in order to make them soluble in organic solvents. Among those synthetic techniques is 1,3-dipolar cycloaddition. In our studies, we used a synthetic protocol that incorporated the use of nitrile oxides as 1,3-dipoles that reacted with the SWCNTs in a [2+3] fashion when heated via conventional methods or microwave promotion. In order to confirm that cycloaddition was realized, FTIR was used to identify the newly formed ester functional group of the desired product. Reaction of the ester functional group of the SWCNT with cysteamine under microwave

conditions formed the targeted thiol capped SWCNT where the presence of the thiol functionality was determined through Raman Spectroscopy. After the thiol capped SWCNT was reacted with gold nanoparticles, TEM was used to verify that the gold nanoparticle successfully attached to the SWCNT.

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COLL 292

Synthesis and properties of the nanostructured polyaniline as a support for horseradish peroxidase immobilization

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In this paper, we reported a simple and fast immobilization of Horseradish peroxidase (HRP) on PANI nanofibers using in situ polymerization. It is found the micelles composed with aniline monomer and HRP can act as the soft templates to form the PANI nanofibers-HRP. HRP could be attached firmly on the PANI without glutaraldehyde which was necessary for the PANI-HRP in the previous literatures. PANI nanofibers-HRP was tested to oxidize the Guaiacum Phenol and Methyl Orange and it was demonstrated that immobilization significantly enhanced the storage stability of the enzyme. When stored at 4°C, no obvious activity loss was observed for the PANI nanofibers-HRP after 6 months while only 20% activity of free HRP was maintained at the same conditions. After 6 times of usage, almost 70% of the initial activity of PANI nanofibers-HRP could be still remained.

COLL 293

Surface chemistry of water-covered Si(001)-2x1: silicon radical versus silanol reactivity

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Water react dissociatively on the Si(001)-2x1 surface, preserving the dimerization. Monohydrides and silanols are present on the surface, together with a low (10⁻² ML) surface concentration of isolated dangling bonds, whose electronic structure is identical to those found on the H-terminated surface.¹ Therefore by analogy the case of the H terminated surface, radical chain reactions (via H jumps) between isolated dangling bonds and pi bonded molecules are expected.² However (i) radical reactions via OH jumps, together with direct reactions with (ii) silanols and (iii) monohydrides must be envisaged. We present here a study of the chemical reactivity of the water-covered Si(001) surface exposed to alkenes, carboxylic acids and aldehydes, using synchrotron x-ray photoemission and scanning tunneling microscopy in combination. While, alkenes likely react via a radical mechanism (H jump), carboxylic acid grafting consumes surface OH and an ester is formed. The reaction of aldehydes is discussed in terms of the formation of (hemi-)acetals or of ethers. Compared with classic organic reactions (esterification, acetal formation) which are slow/reversible, the grafting of aldehydes/carboxylic acids is efficient on the water-covered Si(001)-2x1. This class of high selectivity reactions is a interesting option for the grafting of organic molecules on Si(001), especially for polyfunctional molecules, which generally adopt multiple bonding configurations on the clean Si(001) surface.

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COLL 294

Synthesis and Superlattice of Metal Oxide Nanoparticles

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Metal oxide nanoparticles of Fe₃O₄, ZnFe₂O₄, AlFe₂O₄, and ZnMnFe₂O₄, have been synthesized with adjustable size in different ranges. They are monodisperse and dispersible in organic solvents, such as chloroform, hexane, and toluene; they can be easily transferred into aqueous phase using amphiphilic polymers and small surfactants for biological and environmental applications. The synthesized spherical metal oxide nanoparticles can self-assemble into superlattices in solution through the control of temperature variation rate.

COLL 295

Size Effect Investigation of Palladium Nanoparticles Supported into Silica Colloids as the Catalyst for Suzuki Cross Coupling Reaction

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Palladium nanoparticles (Pd NPs) provide high activity in catalyzing Suzuki cross coupling reaction, which is the most versatile reaction for forming carbon-carbon bond, due to its high surface to area ratio. Silica colloids are used as the support for Pd NPs to provide heterogeneous catalysis for the reaction. Size factor is very important in the activity of the catalyst.

Four different sizes of Pd NPs stabilized by PVP are synthesized using seed-mediated growth method and supported onto silica colloids. Besides that, four different sizes of silica colloids were synthesized as the support of seed Pd NPs. All of the catalysts were used for Suzuki reaction of phenylboronic acid and iodobenzene. The size effect of the PdNPs supported by silica colloids was compared by comparing the turnover number (TOF) of each of the catalyst. We found out that the smaller the size of the Pd NPs, the higher the activity of the catalyst.

COLL 296

Static and Dynamic Surfaces to Control Stem Cell Differentiation

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Traditional *in vitro* stem cell differentiation is controlled via chemical stimuli. However, recent reports have indicated that mechanical stimuli can influence differentiation as well. A number of methods were employed to further elucidate the mechanisms by which such stimuli control human mesenchymal stem cell differentiation: nanostructures (Si nanowires), matrix elasticity (PDMS of varying stiffness), and mechanical force (ultrasound). Additionally, novel surface treatments of materials were investigated to determine their ability to enhance stem cell adhesion and proliferation on a variety of novel surfaces. Differentiation was monitored by standard molecular biology methods (immunostaining, qPCR) as well novel methods including atomic force microscopy (AFM) and ATR-FTIR. These novel material/surface treatments exhibited increased rates of cell adhesion and stem cell differentiation when compared to polystyrene plastic controls. When combined with *in vitro* differentiation monitoring via AFM and ATR-FTIR, this system allows for increased differentiation rates, and increased ease of monitoring differentiation.

COLL 297

Nano-faceted Metal Surfaces: Catalysis and Nano-templates

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In this work, nano-faceted metal surfaces have been used as model catalysts for various reactions and as nano-templates for growth of metallic nanostructures. Faceting of metal surfaces is a form of self-assembly on the nanometer scale and occurs when an initially planar surface of a metal single crystal converts to a nano-faceted surface with "hill and valley" structure exposing new crystal faces on the nanometer scale when covered by gas or metal followed by annealing in vacuum or upon annealing in gas. Annealing Ir(210) in O₂ leads to formation of nano-faceted O/Ir(210) that consists of three-sided pyramids exposing (311), (31-1) and (110) faces on each pyramid, and clean faceted Ir(210) can be routinely prepared in-situ by reaction with hydrogen at 400K. We have carried out a series of reactions on clean planar Ir(210) and clean faceted Ir(210) with different facet sizes to probe for structure sensitivity and size effects on the nanometer scale. Annealing Ru(11-20) in NO₂ produces ridge-like faceted Ru(11-20) surface exposing (10-11), (10-1-1), (01-11) and (01-1-1) faces. Faceted O/Ru(11-20) facilitates growth of Au nanoclusters at room temperature which preferentially nucleate within valleys of the faceted surface. This work is supported by DOE (Contract No. DE-FG02-93ER14331).

COLL 298

Nanopatterns of multidentate adsorbates fabricated through particle lithography: Comparison of surface degradation of alkanethiols versus multidentate thiols using atomic force microscopy

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Multidentate thiol self-assembled monolayers (SAMs) form multiple thiol-gold bonds to the surface which should improve the overall stability of the films. Using atomic force microscopy (AFM) we are investigating the structure and properties of multidentate SAMs in comparison to traditional *n*-alkanethiol SAMs, which have a single thiol link to gold surfaces. Test platforms of thiol SAMs were prepared using particle lithography and investigated under different conditions. Monolayers of traditional alkanethiols were compared side-by-side with multidentate thiols using AFM. The performance of the multidentate adsorbates and stability can be evaluated systematically as a function of the structure, e.g. the nature of the headgroup, junction, and tailgroups. The extent of surface degradation can be viewed directly with AFM images, and significant changes are evident after *ex situ* exposure to heat, light, or chemical reagents. These studies will enable a quantitative evaluation of the resist qualities of multidentate adsorbates.

COLL 299

Directed self-assembly of fibronectin using particle lithography with organosilanes

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An approach will be described for high-throughput patterning of fibronectin using the headgroups of organosilane self-assembled monolayers to achieve spatial selectivity at the nanoscale. By combining particle lithography with organosilane self-assembly, regularly arranged nanostructures can be prepared for immobilizing proteins. For particle lithography, basic bench chemistry steps of mixing, heating, centrifuging and drying were used to rapidly and reproducibly prepare billions of nanostructures with relatively few defects. The organosilane nanopatterns provide a surface template for studies of biological systems, such as for studies of the extracellular matrix protein, fibronectin. The nanopatterns furnish a robust surface platform that can sustain multiple successive measurements with scanning probe microscopy, and may also be useful for mediating surface directed growth of cells. Scanning probe studies will be presented which evaluate the surface conformation of the protein after immobilization. The nanopatterning approach enables fundamental investigations of protein-binding interactions for application in bioassays and biosensor surfaces.

COLL 300

STM Analysis of the Electronic Structure of Isolated Dangling Bonds on Various Doped Water-Saturated Si(001)-2 x 1 Surfaces

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Using scanning tunneling microscopy and spectroscopy (STM/STS), the electronic properties of isolated dangling bond (IDB) defects on variously doped n and p-type water saturated Si(001) – 2 x 1 surfaces are examined. Analysis of the IDB surface density and STM tip height at the IDB defects for samples of different dopant type and concentration provide valuable insight into the reactivity of the unsaturated surfaces, as well as the electronic structure of the IDBs. The information acquired from the topological height maps of the STM images is then correlated to STS curves of the IDB defects on the variously doped sample surfaces. Using this data, further insight is garnered toward an explanation of the IDB charge state, which is neutral for all dopant concentrations except for heavily doped n-type silicon, which is negatively charged.

COLL 301

Functionalization of Titanium Nanoparticles and Titanium Plates

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Titanium Dioxide nanoparticles can be functionalized with a variety of aldehyde, amine, or silane groups under “simple” chemical conditions. The hydroxy groups surrounding the oxidized titanium are susceptible to react with a collection of practical chemicals that allow for antibody and protein attachments. Dopamine, 3,4 dihydroxybenzaldehyde, and APTS have produced consecutive results. Though not in substantial quantities, confirmations of attachment to the Titanium Dioxide nanoparticles were characterized using ¹H, ¹³C-NMR and IR. Techniques and methods were transferred to Oxidized Titanium plates, where X-ray photoelectron spectroscopy was used to quantify surface binding. Surface functionalization of Titanium metal has been investigated to construct reliable ventricular assist devices. Current devices oppose natural biological flow through the tubular structure, presenting problems with specific protein buildup. The goal is to investigate and quantify functionality on Titanium nanoparticles to eventually transfer data and methods to use for alternate antibody and protein attachments to Titanium metal.

COLL 302

Loading of gold nanoparticles and nanoshells into human serum albumin nanoparticles for targeted drug delivery

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Recently, much progress has been made in the use of nanoparticles (NPs) as early detection and treatment options for many different types of cancer and other diseases. Human serum albumin (HSA), the most abundant human blood protein, has been studied as a promising cancer detection and treatment carrier system. HSANP colloids, formed via a desolvation and cross linking method have had major success; with the size of the HSANPs having crucial importance for loading and *in vivo* performance. This research reports an efficient method for preparing, loading and characterizing HSANPs colloids by varying preparation parameters and notably further improving the purifying step, which is key to understanding yield and formation dynamics. Furthermore, the desolvation and cross-linking creation method was employed to encase already formed gold nano-shells (AuNSs) and solid gold nanoparticles (AuNPs) into HSANPs. These relatively non-toxic, metallic gold nano particles offer combinational therapy via imaging and photo-thermal ablation techniques.

COLL 303

Interfacial Tension Measurements at Elevated Temperatures/Pressure

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Research into the interfacial tension of various asphaltenes dissolved in toluene and crude oils at elevated temperatures and pressures required the construction of a special cell. A custom-made heating jacket enabled us to raise the cell to the desired temperature while still allowing for a picture of the drop for determination of drop shape and hence interfacial tension. A special high temperature window was required to withstand both the pressure and allow a photograph of the drop. Two input valves allowed us to input the heavy phase and light phase separately. Once equilibrium had been reached, the light phase would be injected until a satisfactory bubble formed. The change in densities of both phases with respect to temperature needed to be accounted for. Measurements were usually made for one to two hours at 25 °, 50 °, 75 °, 100 °, and 125 °C, with the capability of measurements as high as 175 °C.

COLL 304

Antimicrobial nanoparticles coating of cotton using simultaneously enzymes and ultrasound

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ZnO nanoparticles (NPs) have received increasing attention as antibacterial materials[1]. It has been shown that the antibacterial effect of ZnO depends on the particle size[2]. Enzymatic pre-treatment of cotton fabrics previously showed to improve the uniformity and reduce the size of ZnO NPs, thus increasing their antimicrobial efficiency[3]. Herein, we developed a coating process for cotton fabrics using simultaneously cellulases/ZnO/ultrasound. Uniform coating with high antibacterial activity was obtained in this simultaneous process employing low concentration of ZnO (2mM).

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COLL 305

Simultaneous coating of hybrid bio nanocomposite (Chitosan/Zinc Oxide nanoparticles) using ultrasounds to enhance the antimicrobial activity of Cotton Fabrics

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Synthesis of hybrid material (chitosan/ZnO nanoparticles) was performed using different concentrations of ZnO and chitosan. Cotton fabrics were successfully coated by means of a simultaneous sonochemical deposition of two compounds with intrinsic antibacterial activity, chitosan and ZnO nanoparticles (NPs). The sonochemical process for cotton coating with hybrid antimicrobials was optimised in terms of compounds concentrations, processing pH, time, and solvent used. Considering that high concentration of ZnO NPs renders the fabrics rather hydrophobic without significantly improving further their antimicrobial performance 2 mM ZnO NPs and 0.3 % of chitosan were selected as the optimum concentrations to be used in the simultaneous sonochemical coating process. The hybrid chitosan-ZnO coating material displays higher antibacterial activity when compared to the coatings comprising the individual components as chitosan.

COLL 306

Anisotropic Forces and Adhesion in Gecko Inspired Biomimetic Surfaces

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This research focuses on the advancement of novel biomimetic surface modification based on gecko structures. The gecko's toe uses a fibrillar adhesive system to allow anisotropic friction, thereby allowing it to move on vertical surfaces with ease or even upside down. These structures have been mimicked using polymer microstructures at which point a tribometer is used to measure friction forces as well as the normal force of adhesion. Furthermore, another level of mimicking has inserted tilted structures into the picture, allowing for anisotropic interactions in friction. Current results are comparable to the natural gecko's characteristics. New studies are in progress to observe the efficiency of the synthetic structures in different environments and in scaling the test surfaces. Once realized, these materials would be applicable to those situations in which chemical adhesives are utilized.

COLL 307

Bridged polysilsesquioxane spheres as stabilized UV absorbers for sunscreens

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Compromises to healthy skin are frequently caused by extended exposure ultraviolet (UV) radiation. While commercial sunscreen ingredients are successful at initial protection, they are severely limited in safety and effectiveness due to UV-induced decomposition and skin allergies. Efforts to mitigate ingredient instability involve microencapsulation within a metal alkoxide shell. Unfortunately, leaching can occur, resulting in dangerous skin penetration. Preliminary investigations with bridged-dansyl spheres detail that covalent incorporation of a bridged silsesquioxane is preferred to securely attach the ingredient to the silica matrix and minimize leaching. Additionally, monodisperse spheres are easily prepared, are visibly transparent in cosmetic formulations, and display increased UV stability over that of un-incorporated and pendant silsesquioxane counterparts. Current efforts involve the preparation and first investigation of bridged silsesquioxane analogues of commercial sunscreen ingredients for incorporation within silica spheres. As such, these new ingredients can eliminate the problems associated with current sunscreens.

COLL 308

Surface Modification of Carbon Hard Sphere Via Surface Initiated Atom Transfer Radical Polymerization

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Lubricants play an integral role in the operation of several technologies and in biology also, ranging from moving parts in machinery to the biolubrication of artificial joints. We have found that a colloidal dispersion consisting of easily synthesized highly spherical and uniform carbon particles coupled with surface grafting of polymers that results in a very effective water soluble lubricant with low friction coefficient and excellent surface wear protection. We propose that these particles would increase the overall friction coefficient than without the grafted polymer. These particles use a rolling mechanism similar to nano –or microscale ball bearing under confinement. The effect of several parameters of lubrication including the thickness of the grafted polymer layer, type of polymer grafted, along with the size and porosity of the carbon particles will be presented.

COLL 309

Photocatalytic degradation of 4-chlorophenol: Effects of Ag and Au and its activity in a multi-stage reactor

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Photocatalytic activities of Ag/TiO₂ (Degussa P25), Au/TiO₂ (Degussa P25) and temperature treated TiO₂ (Degussa P25) on the 4-chlorophenol degradation were

studied. A batch-type reactor was used to carry out the reaction with suspended TiO_2 , while a continuous multi-stage reactor was used for immobilized TiO_2 under an irradiation of 11 W low pressure mercury lamp with the wave length of 200-300 nm. From the batch type reactor, the presence of either temperature treated TiO_2 , Ag/TiO_2 or Au/TiO_2 affects insignificantly the 4-CP degradation compared to the photolysis. In contrast, TiO_2 significantly affects the formation/degradation of intermediates, hydroquinone and hydroxyhydroquinone. The presence of Ag and Au does not improve the catalytic activity of TiO_2 in the 4-CP degradation but it affects the degradation of the intermediates. TiO_2 was immobilized on the cylindrical stainless steel mesh by dip-coating with the suspension of TiO_2 (Degussa P25) in methanol and used as the catalyst in the multi-stage reactor unit. The titania on the stainless steel mesh support was found to be well adhered and its activity was still high after the regeneration.

COLL 310

Improved Analysis for Determining Diffusion Coefficients from Short Single-Molecule Trajectories with Photoblinking

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Two Maximum Likelihood Estimation (MLE) methods were developed for optimizing the analysis of single-molecule trajectories that include phenomena such as experimental noise, photoblinking, photobleaching, and translation or rotation out of the collection plane. In particular, short, single-molecule trajectories with photoblinking were studied, and our method was compared with existing analytical techniques applied to simulated data. The optimal method for various experimental cases was established, and the optimized MLE method was applied to a real experimental system: single-molecule diffusion of fluorescent molecular machines known as nanocars.

COLL 311

The interaction of dibenzothiophene with Ag clusters on oxidized and reduced $\text{TiO}_2(110)$

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We have investigated the interaction of dibenzothiophene (DBT) with a $\text{TiO}_2(110)$ surface using temperature programmed reaction spectroscopy and X-ray photoelectron spectroscopy. DBT molecularly desorbs from a reduced surface with a desorption activation energy of 110 kJ/mol. No reaction products were observed, and no residual carbon or sulfur accumulated on the surface. We also studied the effect of metallic silver nanoparticles on the desorption activation energy, as well as the interaction of DBT with

the oxidized surface, and oxidized supported Ag clusters. The results of this work are important in understanding the adsorptive removal of DBT and related compounds from petroleum using supported Ag clusters.

COLL 312

Synthesis and Self-Assembly of Mono-Functionalized Thiophenes

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Self-assembly of thiophene compounds at interfaces can influence the properties of devices with components containing these ubiquitous functional groups, yet this process is poorly understood. Here the influence of substitution on self-assembly of alkylthiophenes is studied to uncover the effects of substitution on the patterns formed by molecules at the liquid/solid interface. Monofunctionalized thiophene derivatives including *N*-octadecyl-2-thiophenecarboxamide, *N*-octadecyl-3-thiophenecarboxamide, *N*-octadecyl-*N'*-2-thiophene-urea, and *N*-octadecyl-*N'*-3-thiophene-urea were generated and the self-assembled monolayers were studied using scanning tunneling microscopy (STM). It is apparent that different moieties and ring-substitution positions influence packing pattern. Attaching amide functional groups at the 2- versus the 3-position affected the orientation of molecules within the monolayer in a manner consistent with a drive toward centrosymmetry. Introduction of urea functionality induced dramatic changes in the molecular conformation and hydrogen-bonding pattern. The monolayers were modeled using molecular mechanics and analyzed using DFT calculations to explore why changes in molecular structure influenced the packing patterns.

COLL 313

Multi-photon photochemistry to map the local fields of plasmonic nanocrescents

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Plasmonic nanocrescents are asymmetric structures with non-uniform, polarization dependent near-field distributions. We investigated the near-field distribution of nanocrescents using localized photo-polymerization. Polymerization of SU-8 photoresist was initiated through two-photon absorption (TPA). AFM was used to visualize the topography of cross-linked polymer relative to gold nanocrescents. Due to the sensitivity of TPA to local intensity, we expected areas of cross-linked polymer to represent the spatial distribution of enhanced fields. After exposure and development of SU-8 coated

nanocrescents, polymerized regions were characterized with AFM and results were compared to scanning electron microscopy (SEM) analysis. We observed a strong polarization dependence of the near-field due to the different plasmon resonance modes which were excited. Regions of polymerized SU-8 were partially correlated with the near-field distributions predicted by simulations. A better understanding of the near-field plasmonic nanocrescents has implications for applications of the structures in sensing and spectroscopy.

COLL 314

Fabrication of Poly(glycerin)-b-Poly(ϵ -caprolactone) Polymer Vesicles in Capillary Microfluidic Devices

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We introduce a versatile microfluidic approach for fabricating monodisperse polymersomes with a new type of biocompatible and biodegradable block copolymers, polyglycerin(PG)-*b*-poly(ϵ -caprolactone)(PCL). We use double emulsions as templates for the assembly of amphiphilic PG-*b*-PCL block copolymers into a vesicle structure. We observe how molecular architectures of block copolymer affect formation polymer vesicles in microfluidic devices. Depending on the block ratio between PG and PCL, the dewetting of template double emulsions can be controlled. To observe the ability of our polymersomes to encapsulate hydrophilic biomolecules, we encapsulate dextran probes in the core of polymersomes. In response to an osmotic pressure, the polymersomes break and release the probes. The vesicle system fabricated in this study provides a method for drug encapsulation and releasing and may potentially be applied in the fields of cosmetics, dermatology, and pharmaceuticals.

COLL 315

Photonic blocks: templated colloidal crystals

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Inverse opals are highly ordered, porous materials consisting of the negative space in a colloidal crystal. Their high periodicity gives them color, as these materials behave as three-dimensional photonic crystals. We investigated the use of doctor blading to template colloids and a silica precursor into pre-made molds, allowing for the formation of individual photonic crystal pieces. The shape of the mold was varied to change the packing of the colloids, identified by electron microscopy. These changes were then analyzed with optical spectroscopy to identify the effect of substrate geometry on the resulting optical properties of these photonic blocks.

COLL 316

Solution self-assembly of multidentate organothiols on Au(111) studied in situ using scanning probe microscopy

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The solution self-assembly of multidentate organothiols onto Au(111) was monitored *in situ* using time-lapse scanning probe microscopy (SPM). For regular *n*-alkanethiols, densely-packed monolayers typically are formed from dilute solutions within an hour or less; however, self-assembled monolayers (SAMs) of bulkier multidentate thiols were found to assemble more slowly. A clean gold substrate was first imaged in ethanolic media. Next, a solution of multidentate thiol was injected into the liquid cell. As time progressed, molecular-level details of the surface changes at different time intervals were revealed by high resolution SPM images. Nanoshaving and nanografting protocols were used to investigate the orientation of adsorbed molecules. Since the dimensions of *n*-alkanethiols have been well-studied, the thickness of the multidentate thiol film was also evaluated by referencing the heights of *n*-alkanethiols as an *in situ* molecular ruler. Multidentate adsorbates attach to surface through multiple linkers which should provide enhanced stability compared to monothiolated SAMs.

COLL 317

Solid-liquid surface functionalization of biopolymeric platforms with plant-derived polyphenols

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This work reports a straightforward approach for covalent functionalization of solid biopolymeric platforms with plant-derived flavanoid-based antioxidants in order to generate materials with improved antioxidant and antimicrobial properties. The novelty of this approach consists in the use of thiolysis - a common analytical method for proanthocyanidins characterization – in a heterogenic phase reaction to covalently functionalize natural macromolecules such as chitosan with bioactive phenolic moieties. It is known that proanthocyanidins undergo depolymerization in acid medium, where in the presence of nucleophiles form stable flavan-3-ol derivatives. Based on this reaction, flavan-3-ol moieties from polyphenol extract of *Hamamelis virginiana* are incorporated covalently on previously thiolated chitosan matrix. The phenolics-functionalized chitosan possess improved antioxidant and antimicrobial properties *in vitro*

COLL 318

Determination of surface tension and its components of aqueous solutions using liquid-liquid interfacial tensions

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The purpose of this study is to provide a method that can determine surface tension and its components of aqueous solutions. We hypothesized that lower interfacial tensions between the aqueous solution and probe liquids would allow us to obtain more accurate surface tensions. One reason is that the lower interfacial tension would likely provide a smaller driving force for the solutes to transport to or from the water/oil interface. To verify our hypothesis, the surface tensions of several aqueous solutions: water, 3.5 wt. % salt, 30 wt. % sucrose, phosphate buffered saline, and a cell culture medium were determined. Probe liquids of benzaldehyde(BA), ethyl acetate(EA), ethyl ether(EE), benzene(BZ), and octane(OC) were selected based on their interfacial tensions with water and their polarity. In general, three probe liquids are needed to solve for the Lifshitz – van der Waals and acid/base components of the surface tension. Four combinations of the probe liquids were compared: BA-EA-EE, BZ-EA-EE, OC-EA-EE, and OC-BZ-EE, based on a sensitivity analysis with a 5% of error to the interfacial tensions of water and each of the probe liquids. Experimentally, the pendant drop method was utilized to determine the interfacial tensions. For water, due to the absence of solutes, all four combinations lead to similar values of surface tension and its components. However, when the solutes are presented, the values varied with the combination of the probe liquids used. More accurate values were indeed found to be resulted from the combination (i.e. BA-EA-EE) that had lower interfacial tension with water.

COLL 319

Application of scanning probe-based nanolithography for studies of multidentate thiol self-assembled monolayers formed on Au(111)

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Although detailed investigations of monothiolated self-assembled monolayers (SAMs) have been reported, few studies have been accomplished for bidentate or tridentate thiol adsorbates. One may predict that bulkier multidentate SAMs would exhibit differences for the kinetics, stability and surface organization in comparison to n-alkanethiols. We are combining liquid imaging with scanning probe-based nanolithography to enable side-by-side imaging of the surface structures of multidentate adsorbates versus n-alkanethiol SAMs (i.e. film thickness, periodicity). By increasing the force applied to the probe, selected small regions can be shaved away to expose the

substrate. This furnishes a local measurement of film thickness, referencing the uncovered patches as a baseline. Using a liquid sample cell, fresh reagents can be introduced to the system and step-wise surface changes before and after nanofabrication can be monitored *in situ*. With a liquid environment studies of surface reactions can be accomplished with molecular views using time-lapse imaging.

COLL 320

Dynamics of nanoparticles in non-Newtonian aqueous dispersions

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The transport properties of nanoparticles in soft complex media are relevant for polymer and hydrogel nanocomposites but are still poorly understood. We use single-particle tracking to measure the diffusional dynamics of nanoparticles in non-Newtonian aqueous polymer solutions, which serve as models of viscoelastic porous media. We track the motion of polystyrene nanoparticles of diameter 400 nm in aqueous solutions of hydrolyzed polyacrylamide whose radii of gyration are comparable to the diameter of the nanoparticles over a wide-range of dilute and semi-dilute concentrations. At all concentrations, the mean-square displacement (MSD) of nanoparticles at long times is linearly proportional to time, indicating diffusive motion. The viscosity extracted from the MSD systematically varies with polymer concentration but is smaller than the zero shear rate viscosity measured at each polymer concentration using bulk rheometry, indicating that the dynamics cannot be explained in the context of microrheology of viscous solutions.

COLL 321

Influence of clay minerals on the mobility of positively charged nanoparticles in soil

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In order to understand how the mobility of positively charged nanoparticles is influenced by the clay minerals in a soil environment, atomic force microscopy (AFM) was used to observe the interactions of swelling clays with TiO₂ nanoparticles. By measuring the swelling changes in individual quasi-crystals of a clay mineral, which were exposed to an aqueous suspension of nanoparticles of various sizes, the degree to which different types of nanoparticles may be incorporated into the interlayer regions of the clay minerals was determined. The behavior on the nanoscale was correlated with mobility in a soil environment in a series of column experiments.

COLL 322

Nanostructured films of octadecyltrimethoxysilane prepared on indium tin oxide substrates using particle lithography: Control of surface coverage and density

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We have developed a method for creating organosilane nanostructures on indium tin oxide (ITO) using particle lithography and immersion. Glass substrates with ITO films of different thickness and corresponding resistivity were coated with mesospheres and immersed into silane solutions. Silica mesospheres provide a surface mask to prepare periodic arrangements of billions of regular nanostructures with relatively few defects. These spaces can then be further modified to create islands of desired chemical functionalities such as with a second silane using steps of surface-initiated polymerization. The masks were removed by solvent rinsing with sonication and then immersed into a second silane to create the nanoislands within the matrix. Samples were analyzed using contact and tapping-mode atomic force microscopy to evaluate the height, arrangement and geometries of the nanostructures. The nanostructures provide a foundation for chemical patterning or for molecular-level studies of the conductive or photophysical properties of samples.

COLL 323

Utilizing fluorescence spectroscopy to investigate the cholesterol induced liquid ordered phase formation in liposomes

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The liquid ordered domain has been shown to participate in signal transduction and protein targeting as in Alzheimer's Disease (AD) progression. These domains result from cholesterol induced phase changes with properties intermediate of the liquid crystalline and the liquid gel phase and have been verified to exist in the plasma membrane outer leaflet. This phase can be identified using fluorescently tagged lipids that probe membrane environments. The behavior of a fluorescent probe will either indicate ordered or disordered regions. Dipalmitoyl-phosphoethanolamine-N-(7-nitro-2-(1,3-benzoxadiazol-4-yl) or 1-oleoyl-2-(12-(7-nitro-2-(1,3-benzoxadiazol-4-yl)amino)dodecanoyl)-phosphoserine were incorporated into liposomes containing various phospholipid:cholesterol ratios. The composition of the liposomes can be altered to contain different lipids or non-lipid components including Beta Amyloid protein, a major constituent of plaques resulting from AD progression. Dipalmitoylphosphatidylcholine/cholesterol liposomes were used as method validation while dipalmitoylphosphatidylserine/cholesterol liposomes were used to investigate domain formation in the inner leaflet. Liposome data was compared to both AFM images and Langmuir monolayers.

COLL 324

Synthesis of Au/Ag-CdS Hybrid Nanostructures as Efficient Photocatalysts

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Metal-semiconductor hybrid nanostructures have attracted considerable attentions due to their unique photophysical and photochemical properties. These properties are closely associated with not only the size and shape of each component, but also the interface or interparticle spacing between the two components. Herein, we report a synthetic approach to control the architectures of the Au/Ag-CdS hybrid nanostructures. This approach allows for precisely tuning the size of the Au/Ag and the aspect ratio of the CdS in a Janus structure. The photocatalytic activities of these nanostructures are studied by the photodegradation of the organic dyes. We then correlate the morphologies of these hybrid nanostructures with their optical properties and photocatalytic activities.

COLL 325

Fundamentals of Ligand Exchange on Gold Nanorods

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Gold nanorods have gained interest in the recent years due to their numerous potential plasmonic applications. In order to fully exploit their potential, it is however necessary to functionalize the surface of gold nanorods by replacing the native CTAB (cetyl trimethylammonium bromide) bilayer. These ligand exchange reactions often require the addition of a cosolvent, such as acetone, in order to facilitate the exchange. However, not much is known about the solution properties following cosolvent addition.

Herein, the effects exerted by the addition of acetone on the CTAB bilayer and on the nanorods were investigated. The properties of the CTAB micelle were analyzed by surface tensiometry and those of the nanorods by optically investigating their aggregation behavior at variable acetone and CTAB concentration. It was found that at high acetone concentrations the nanorods aggregated but did so following an interesting and unexpected behavior.

COLL 326

Antioxidation properties of cerium oxide nanocrystals depending on nanocrystal diameters and surface coatings

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In this study, we quantitatively studied the effects of the diameter and surface coating of monodisperse cerium oxide nanocrystals on their reactivity towards H_2O_2 . These materials are formed in organic solvents by the high temperature decomposition of cerium precursors, and subsequently phase-transferred into water using amphiphilic coating agents. Quantitative analysis of the antioxidant capacity of nanoceria using GC-MS and a luminol test revealed that two moles of H_2O_2 reacted with every mole of cerium (III), supporting the hypothesis that the reaction proceeds via a Fenton-type mechanism. Smaller diameter cerium oxide nanocrystals have more cerium (III) and thus are more reactive towards H_2O_2 ; over a period of several weeks, the resulting cerium (IV) returns to cerium (III) and the nanocrystals can be used again to react with peroxide. If the surface coatings were in excess of 2 nanometers thick, the samples could not undergo more than a few redox cycles before precipitating. In contrast, nanoscale CeO_2 coated with a very thin bilayer provided colloidally stable material that could undergo repeated redox cycling over 6 months and was able to reduce excess of H_2O_2 more than 20 times. Finally, oleic acid-coated nanocrystalline ceria had nine times higher antioxidant capacity than Trolox in an oxygen-radical absorbance capacity (ORAC) assay. These data suggest that appropriately derivatized nanocrystalline ceria could serve as a scavenger for radical species in biological media.

COLL 327

Antimony and arsenic partitioning in contaminated streambed sediment of a semi-arid creek

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Streambeds contaminated by mining and smelting activity are often significant sources of contamination to river systems due to retention of heavy metals in streambed sediment. Streambed sediment and water chemistry conditions, including pH, ionic strength, and redox, regulate metal release. In this study, sequential extraction was applied to sediment cores collected from a semi-arid creek impacted by antimony (Sb) smelting activity, to determine the specific sediment fractions retaining Sb and arsenic (As), and the potential for metal release. Results showed the majority of total Sb and As concentrations were associated with poor crystalline iron (Fe) oxides in the sediment. Antimony and As release from this fraction is relatively stable under measured stream pH and salinity conditions, but metals may become available if changes in these parameters occur. Pore water was analyzed for determination of observed distribution coefficients for Sb and As, and were found to decrease along depth.

COLL 328

Giving molecules the squeeze: The effects of organic lubricants on the interactions between surfaces with nanoscopic curvature studied by molecular dynamics

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Understanding the dynamics and mechanics of molecular films on surfaces with nanoscopic curvature is critical to understanding nanoparticle dispersion and catalysis, as well as the effects of organic lubricants at solid-solid interfaces which are dominated by asperity contacts. Past studies employing spectroscopy, atomic force microscopy, and molecular dynamics have focused on the effect of surface curvature on the properties of self-assembled monolayers derived from organosilanes, using nanoparticles as model surfaces with tunable surface curvature. To understand how organic lubricants behave at asperity contacts, contact simulations of asperity surfaces, i.e. nanoparticles, with organic films and organic lubricants, have been conducted to study their effects on the contact mechanics and surface forces, pressures, and strains at asperity contacts in molecular detail. The use of nanoparticles as model surfaces facilitates extension of this information to systems including metal oxide nanoparticles and quantum dots, in particular the effects of capping layers upon their properties.

COLL 329

Adsorption of loaded polymeric micelles on silica surface

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This study focuses on adsorption and removal of drug-loaded polymeric micelles on and from silica surface. It is found that the adsorption process for this system is only partially reversible, and most of the adsorbed particles do not desorb from the silica surface even upon rinsing with a large amount of water for long time. The adsorption rate constant decreases with increasing particle size. Some fraction of the adsorbed particles can be removed via rolling or sliding, which is generated by hydrodynamic forces acting parallel to the surfaces. The removal rate constant increases with increasing particle size.

COLL 330

Optimization of the r2 relaxivity dynamics for iron oxide based magnetic nanoparticles depending on their sizes, coatings, and types

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In this work, we have prepared size controlled iron oxide (Fe_3O_4) nanoparticles ranging from 4 to 40 nm and different types of ferrite nanoparticles (e.g. AlFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , MnFe_2O_4 , and MnZnFeO_4). These size tunable iron oxide based nanoparticles were transferred to water using oleic acid (OA), octylamine modified poly (acrylic acid) (PAA-OA), Poly (maleic anhydride-alt-1-octadecene) (PMAO), PMAO-poly(ethylene glycol) (PEG) (PMAO-PEG), and lauryl acrylate (LA)-poly 2-acrylamido-2-methylpropane sulfonic acid (PAMPS) (PAMPS-LA). The relaxivities of hydrated iron oxide magnetic nanoparticles, especially r_2 ($1/T_2$), were optimized and examined depending on their particle diameter (d), average molecular weight (Mw) of phase transfer agents, and types; the r_2 relaxivity of 35 nm iron oxide capped oleic acid was $510 \text{ S}^{-1}\text{mM}^{-1}$. Moreover, *in vitro* cell toxicological studies revealed that various polymer coated iron oxide based T2 contrast agents had no significant effect on human dermal fibroblasts (HDF) even at high concentration (e.g. $6000 \mu\text{M}$). By designing the relaxivity dynamics with their sizes, surface coatings, and types, it will give an efficient T2 iron oxide MRI contrast agents offering high r_2 relaxivity.

COLL 331

Spectroscopic studies of reversible adsorption to functionalized solid/liquid surfaces

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Silica substrates have been functionalized with dendrimers having specific compositions for the express purpose of reversibly removing regulated organic contaminants from aqueous solutions. These chemically tailored surfaces have been characterized using XPS and surface specific vibrational spectroscopy (VSFS). The first generation of these materials uses covalently attached cyclodextrins to bind aqueous phase aromatic solutes including phenols and chlorobenzenes. Bulk Raman studies show that inclusion complexes are formed between β -cyclodextrin and these analytes. Furthermore, fluorescence data show increased quantum yields and longer emission lifetimes for fluorescent analytes when bound by the cyclodextrin. VSFS data from the functionalized surfaces show that a silica surface covered with covalently attached β -cyclodextrin reversibly adsorbs p-cresol within minutes. Collectively, these experiments provide a strong foundation that can be used to rationally design new generations of materials for environmental remediation applications.

COLL 332

Nonlinear studies of adsorption to polar and charged solid/liquid interface

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Resonance enhanced second harmonic generation (SHG) was used to examine the effect of surface charge on adsorption to silica/aqueous interfaces using para-nitrophenol (pNP). pNP adsorption to silica surfaces from an acidic solution (pH = 1,5) is characterized by SHG spectra showing a single excitation wavelength (310 nm) that is measurably blue-shifted from the bulk aqueous limit (at 318 nm). ΔG_{ads} of pNP to the silica/aqueous (pH 1,5) interface is ~ 25 kJ/mole. At higher pH (pH > 7), SHG spectra show two excitation wavelengths at 310 nm and 330 nm that are interpreted in terms of pNP sampling two different solvation environments. The longer wavelength species is assigned to pNP sharing its proton with a deprotonated $-\text{SiO}^-$ surface group. Using SHG field strength as a measure of surface population, both species have ΔG_{ads} values of ~ 22 kJ/mol and these adsorption energies appear to be independent of pH (above pH 7).

COLL 333

Phase behavior and electrophoretic deposition of LPEI-PAA complexes

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Linear poly(ethyleneimine) (LPEI) and poly(acrylic acid) (PAA) were mixed to create polyelectrolyte complexes. The phase behavior of these complexes was studied over the pH range from pH 4.0 to pH 6.0 to determine the mixing ratio at which complexes were no longer soluble and formed solid precipitates. It was found that in this pH range precipitation occurred only when a molar excess of PAA was present. Multilayers of PAA and soluble, charged complexes were formed by mixing LPEI in molar excess with PAA were also prepared to study complex behavior. The multilayer was produced by alternately dipping an indium-tin oxide (ITO) coated glass slide in solutions of the complexes and PAA. A voltage was applied to the substrate to aid in the deposition of the oppositely charged LPEI rich complexes or PAA and to study how the complexes behaved under an applied potential.

COLL 334

Effect of Oxygen in Admicellar Polymerization of Silica Particles in Forming Polystyrene or Poly(methyl methacrylate) Thin Film

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The effect of oxygen on the reaction kinetics of and polymer formed through admicellar polymerization on silica particles was studied. The system consists of cetyltrimethylammonium bromide (CTAB) as the surfactant template, styrene or methyl methacrylate (MMA) as the monomer and azoisobutylnitrile (AIBN) as the free radical initiator. Different techniques of oxygen purging using direct bubbling or freeze-pump-thawed cycles were examined and the formed polymer was compared. Polymer films were extracted and characterized using Fourier Transform Infrared (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography (GPC). The results showed that effect of purging out the oxygen significantly increased the initiator efficiency resulting in the formation of high molecular weight and low polydispersity thin polymer films. Surface characterization using Atomic Force Microscopy (AFM) showed more uniform polymer coverage. This study addresses an alternative choice of PMMA as a “green” polymer thin film and the minimal use of toxic radical initiator in obtaining a better product, providing us a more environmental friendly surface modification technology.

COLL 335

Synthesis and tunability of silver gallium sulfide nanocrystals

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Bandgap tunability of semiconductor nanocrystals is an area of much active research. Traditionally changes in emission wavelength are observed as an effect of particle size and quantum confinement. Recently, it has been shown that emission wavelength may also be tuned by varying the composition in I-III-VI semiconductor nanocrystals. In this work, we present findings on the bandgap tunability of AgGaS₂ nanocrystals by altering the stoichiometry of silver and gallium present in the final crystal structure. Composition was controlled by varying precursor ratios during synthesis. The particles were characterized by photoluminescence to determine the emission wavelength, TEM for particle size and shape, and XRD to find the resulting crystal structure.

COLL 336

Rapid fabrication of hollow microspheres with a hybrid nanoscale double-shelled structure

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Hollow microspheres have received significant attention due to their potential applications such as controlled drug release, chemical sensing, encapsulation, energy storage, catalysis and imaging. Several approaches, including hard or soft templates

methods, have been applied to synthesize hollow microspheres. In the present work, we demonstrate a novel approach to synthesize hollow microspheres where a silica shell is created rapidly through silica condensation at the aerosol droplet's gas-liquid interface, locking in chemical constituents in the interior. This is achieved using an aerosol based process where we have exploited salt bridging concepts to lock the surfactant CTAB and sucrose together with iron oxides in the interior of a droplet while a silica shell is allowed to form on the droplet surface. Subsequent pyrolysis process results in a buildup of internal pressure forcing carbon formation as a second inner layer which is attached to the silica shell. This new assembly method is expected to be a common approach to fabricate various hybrid double layer hollow microspheres with unique potential properties. In addition, the integration of magnetic iron oxide particles into the shells opens up further opportunities in magnetic stimuli responsive materials.

COLL 337

Microwave-assisted synthesis of triangular silver nanoplates: Influence of seed clusters

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Silver nanoparticles were produced by an aqueous synthesis using a variable frequency microwave reactor system, where silver nitrate is reduced by polyvinylpyrrolidone, with no other reagent present. Here, microwave-assisted synthesis reduces reaction time significantly (from days to minutes) compared to conventional heating methods, even if the nominal reaction temperature is identical. Thermodynamic nanocrystal growth mechanisms predict that the only shape present after microwave synthesis should be spheres due to the ultrafast evolution of particles, but a bimodal population of triangular nanoplates and spheroidal particles was obtained under microwave conditions. The development of triangular nanoplates provides further evidence that, in the absence of other shape directing agents, nanocrystal shape is largely dictated by the configuration of the initial seed clusters.

COLL 338

Gold nanoparticles in the mitochondria

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The use of gold nanoparticles (Au NPs) has been gaining traction in the arena of biomedical imaging and sensing due to their large scattering coefficient and low toxicity. The versatility of Au NPs is also enhanced by functionalizing them with various ligands. Previously, we have shown that Au NPs can be coated with a hybrid bilayer of

phospholipids of phosphatidylcholine and phosphatidylserine. Here, we study the biocompatibility of these hybrid Au NPs with prostate cancer cells (PC3) and human dermal fibroblast cells (HDF). Interestingly, while studies show that hybrid Au NPs enter the cells via an endocytotic route, TEM images suggest that these Au NPs ultimately ended up in the mitochondria, causing its disruption over longer incubation times.

COLL 339

Soft networks of crosslinked gold nanoparticle films formed at an air-water interface

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The structural dynamics of thin films of surfactant molecules can be characterized by their behavior in a Langmuir trough, where the molecules reside at the air-water interface. Less common is the use of a trough for the fabrication of organized two-dimensional arrays of alkanethiol-capped gold nanoparticles. Here, hydrophobic nanoparticles are introduced to the air-water interface as a solution in hexanes; as the solvent evaporates, the floating nanoparticles can be compressed into a close-packed monolayer. Preliminary studies have explored the relationship between film morphology and the length of the hydrocarbon chain; it has been found that nanoparticles capped with alkanethiols having chain lengths $< C16$ form poorly organized films with low collapse pressures. We have found such films are greatly improved when crosslinked by alkanedithiols prior to compression within the trough. The resulting soft networks of nanoparticles exhibit increased collapse pressures and remain intact when transferred to a solid substrate.

COLL 340

Chemical ordering in metal-based composite nanocrystals

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The production of nano-scale materials with predictable and reproducible composition and morphology has been a continuing problem for researchers in nanomaterials. Hyper-branched polyethyleneimine, as a polymer scaffold, was complexed in aqueous solution with Co^{2+} and Pt^{4+} in various ratios to form metal alloy Co_xPt_{1-x} nanomaterials. Chemical reduction of the scaffold-metal precursor complex results in the kinetically-favored crystalline, amorphous phase. This research examines whether photo-reduction of the precursor complex results in a thermodynamically-favored chemically-ordered crystalline phase, while also achieving a narrow size distribution. As-prepared sample and grain-by-grain measurements are conducted in order to ascertain the effect of chemical versus photo-reduction and molar ratios of precursor compounds on

composition and structure. Preliminary results show that the size control previously reported in the literature is achievable through photo- and chemical reduction, and that the polymer prevents aggregation in solution.

COLL 341

Swelling behavior of thin polymer films monitored by ellipsometry and nanomechanical response

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Poly(hydroxyethyl methacrylate), PHEMA, swells in water, making its application in the production of soft contact lenses one of the most relevant. PHEMA thin films were spin-coated from 30g/L solutions prepared in methanol onto Si wafers or Si microcantilevers. The swelling behavior of such films was investigated by ellipsometry (wavelength: 632.8 nm) and nanomechanical response. The ellipsometric angles were measured under relative humidity (RH) of 25%, 62%, 70% and 96% and 24±0.5 °C. PHEMA's mean index of refraction values decreased exponentially from 1.516±0.005 (25% RH) to 1.476±0.009 (96% RH). The mean thickness values increased exponentially from 57.9±0.5 nm (25% RH) to 63.2±0.8 nm (96% RH). Microcantilever resonance frequency was recorded at RH from 0-80%. A frequency shift of 0.2 kHz was detected, corresponding to a 4% increase of mass. Microcantilever deflection was recorded at RH cycles (0-82% RH). The MC moved downwards as RH increased, causing deflections of ~60±5 µm.

COLL 342

Design, fabrication and characterization of mechanically patterned polydimethylsiloxane substrates using thiol-ene chemistry

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Polydimethylsiloxane (PDMS) is an important material with promising applications in biomedical engineering. The objective of this research is to fabricate mechanically patterned PDMS as a substrate to study cell mechanotaxis, which refers to the phenomenon that cells migrate to stiffer regions on a substrate where a stiffness gradient is present. Photo-initiated thiol-ene chemistry using thiol- and vinyl-functionalized PDMS prepolymers allows us to impart temporal and spatial control of Young's moduli across PDMS substrates. Atomic force microscopy (AFM) is used to characterize surface modulus of crosslinked PDMS substrates using various

mechanical models. The Johnson-Kendall-Roberts (JKR) model appears to be the one that results in the best match between surface and bulk moduli. The effect of hydrophilization treatment of the PDMS substrates on surface modulus will also be evaluated by AFM force measurements.

COLL 343

Generating Randomly Rough Surfaces and Roughness Gradients using Electrochemical Deposition

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A novel approach to reproducibly generating randomly rough surfaces over large areas and generating surface roughness gradients is presented. By tuning the electrochemical deposition potential for silver onto an electrode, the island nucleation density can be systematically varied resulting in thin films of different roughness. We find that the potential range that significantly influences the surface roughness also corresponds to a reaction/mixed-controlled deposition regime. The roughness can be replicated onto other moldable materials, thus enabling future studies involving the effect of surface roughness.

COLL 344

Nuclear-Targeted Gold and Silver Nanospheres: A Fundamental Study in Cellular Death Mechanisms

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Plasmonic nanoparticles (NPs) have become a useful platform in the biomedical field due to their potential use in disease diagnosis and treatment. It has previously been reported that nuclear-targeting gold (AuNSs) and silver (AgNSs) nanospheres both induce DNA damage and an increased cytotoxicity in cancer cells; their perturbation of the cell cycle differs. In the present work, we investigated the cellular death mechanism induced after human oral squamous cell carcinoma (HSC-3) cells were treated with nuclear-targeting AuNSs and AgNSs. Through flow cytometry, confocal microscopy, and western blotting, we were able to analyze the effects of targeted NPs treatment at the intracellular level. Results suggest that nuclear-targeted AgNSs caused greater apoptotic populations when compared to AuNSs due to the generation of reactive oxygen species (ROS). Current studies investigating possible apoptotic pathways triggered after treatment with nuclear-targeted AuNSs and AgNSs are also discussed.

COLL 345

Construction of a Simple Millifluidic Reactor for the High-throughput Synthesis, Functionalization, and Monitoring of Gold Nanospheres and Nanorods

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The controlled synthesis of many functionalized nanoparticles above the milligram scale continues to be a significant challenge. The synthesis of functionalized nanomaterials in flow reactors provides a viable approach to circumvent the shortcomings of traditional batch synthesis, providing improved control over product properties and the potential for high-throughput synthesis. Here, we demonstrate the construction and operation of a millifluidic reactor assembled entirely from commercially available components. This reactor facilitates the high-throughput synthesis of a variety of functionalized gold nanoparticles (AuNPs), including gold nanorods (AuNRs) with controlled aspect ratios. The high-throughput synthesis approach facilitated by the flow reactor permits the rapid synthesis of AuNRs on the gram scale. The reactor can also be adapted to enable high-throughput surface functionalization of AuNPs and real-time monitoring of AuNP growth. We have used the flow reactor to facilitate the synthesis of a library of functionalized AuNPs for the study of how AuNP surface chemistry influences their interactions with cell membranes.

COLL 346

Preliminary evaluation of the impact of silver nanoparticles on the germination and growth of radish seeds exposed to lead and aluminum

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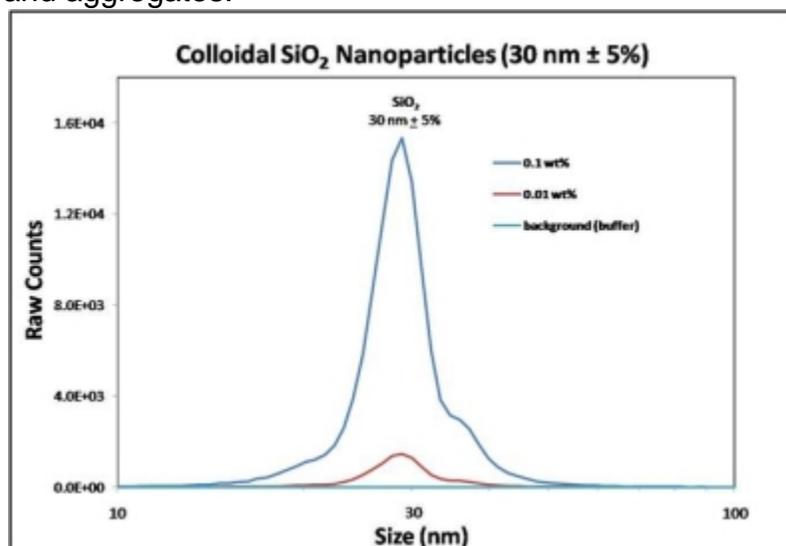
The indiscriminate disposal of metals in the environment is threatening for the conservation and management of ecosystems, biodiversity, agriculture, and health issues. The use of silver nanoparticles (AgNO_3) in bioassays is an innovative strategy to: assess plants as environmental biomonitors for metals, such as lead and aluminum, and analyze the potential use of silver nanoparticles in bioremediation. Radish seeds, characteristically with rapid growth and high adaptability, were tested for germination and early growth rate on laboratory controlled conditions and open field conditions using spherical silver nanoparticles of approximately 20 nm. Solutions with different proportions of lead and aluminum and nanoparticles showed an increase and decrease in the germination rate. However, growth rate was significantly inhibited. Further studies will explore the potential use of silver nanoparticles for bioremediation and compare the impact of silver nanoparticles with other nanoparticles such as zinc and cadmium.

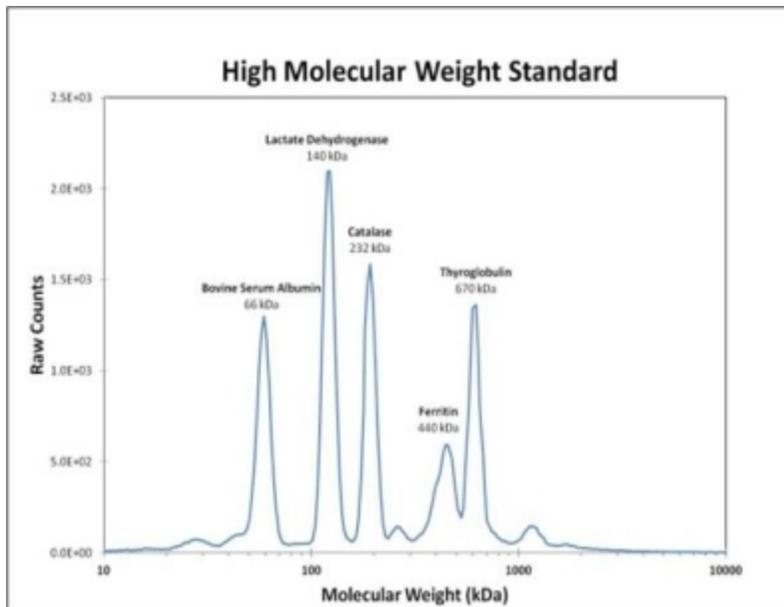
COLL 347

Nanoparticle and Protein Size Analysis by LiquiScan-ES

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LiquiScan-ES is a versatile ion mobility spectrometry system that relies on first-principle analysis to determine the size and molecular weight of nanoparticles, macromolecules, and complexes in the range of 2.5 nm to ~ 1 μm (8 kDa to > 80 MDa). Droplets produced by an electro sprayed analyte solution are neutralized, resulting primarily in singly charged ions. The sizing of the ions in a gaseous state is accomplished by differential mobility analysis in an electrical field and subsequent detection by condensation particle counting. Samples can be analyzed rapidly and reproducibly with high resolution, sensitivity, and accuracy in comparison with standard analytical methods. This technique is also independent of the optical properties of the analyte and solvent and can produce an accurate measurement of multimodal distributions. Indeed, LiquiScan-ES has proven to be a valuable tool for analyzing and quantifying nanoparticles and macromolecules such as proteins, DNA, carbohydrates, polymers, and aggregates.





COLL 348

Use of silver nanoparticles to reduce *Escherichia coli* and *Enterococcus* from waste water

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Microbiological contamination in natural and potable waters remains a pressing global issue that our society still facing in the new millennium. Thanks to the accelerated growth in the field of the nanotechnology new strategies using nanometallic particles are been investigated as an alternative use of regular antimicrobial. Silver is well known for its antimicrobial characteristic. This project investigates the effect of silver nanoparticles and nanoprisms on *Escherichia coli* as a model for Gram-negative bacteria and *Enterococcus faecalis* as a model for Gram-positive bacteria as a way to corroborate the result obtained in other investigations. Bacteriological tests were performed in a form that reassembles an antibiogram. It is important not to just come up with a solution but to come up with a cost effective solution, it's why we synthesized our silver spherical nanoparticles and our silver nanoprisms by using nanomaterial's that can be prepared in a simple and cost-effective manner.

COLL 349

Comparative study of the antimicrobial effect of different antibiotics mixed with CdS and bimetallic Ag-Au core-shell nanoparticles in *Staphulococcus aureus* and *Escherichia coli*

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Due to the rapid emergence of resistant microorganisms to different antibiotics, we have to resort other areas of science to create new antimicrobial agents. Nanotechnology has a great impact in this area since nanoparticles can improve the antimicrobial effect of antibiotics. The aim of this study is to develop new and effective methods against resistant bacteria. The antibacterial effect was evaluated using CdS and bimetallic Ag-Au core-shell nanoparticles with different concentrations of the following antibiotics: Gentamicin, Cephalexin and Ciprofloxacin. Antibacterial activities against *Escherichia coli* (ATCC 10536) and *Staphylococcus aureus* (ATCC 25923) were investigated by determining the minimum inhibitory concentration (MIC). The results showed that some nanoparticles are effective in growth inhibiting in these microorganisms by increasing the effectiveness of the antibiotic. A previous study revealed that antibiotics mixed Ag, Au, and ZnO nanoparticles increased the potential of a specific concentration of antibiotics while in others it decreased.

COLL 350

Ionic liquid and cation effects on the synthesis of silver iodide nanoparticles

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An ionic liquid of either 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄), or 1-butyl-3-methylimidazolium hydrogen sulfate (BMImHSO₄) was added to a water-in-oil micro emulsion to observe the effect of ionic liquids on the kinetics of forming silver iodide nanoparticles inside a reverse micelle template of Polyethylene glycol tert-octylphenyl ether (Triton X-100) surfactant. The objective was to evaluate the effectiveness of ionic liquids to form nanoparticles of uniform size. A time driven uv-vis absorbance measurement was used to approximate the relative population of nanoparticles with a size that corresponds with an excitonic peak of 420 nm. The results show a faster increase in the relative population of nanoparticles as ionic liquid was used. It is suspected that the presence of ionic liquids allowed a faster rate of intermicellar exchange of precursor ions which coupled with the ionic liquids.

COLL 351

Determination of heavy metals in water using silver, gold and semiconductor nanoparticles

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Nanomaterials present novel properties with the possibility of new contributions in the forensic science field. Determination of drugs, xenobiotics and heavy metals are critical in the elucidation of poisoning and death. Nanomaterials can be applied to the analysis of trace evidence; gunshot residues, heavy metals and halogenated organics materials. In this work we use nanostructure materials for detection of toxic agents in water samples. We successfully achieved the synthesis of Ag, Au, ZnO and CdS nanoparticles using microwave technology. In this work we summarized the nanoparticles interactions with water samples containing different quantities of heavy metals and chlorinated compounds. Characterization of these materials was performed using UV-Vis spectroscopy, IR, TEM and XRD techniques. Our study will contribute in the elaboration of new simple methods, providing better detection limits.

COLL 352

Functionalization and characterization of noble metals nanoparticles with antibiotics

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Metal noble nanoparticles such as: gold, silver and copper have been used in several biological, technological and medical applications. Our research focused in the synthesis of noble metals nanoparticles functionalized with antibiotics. We prepared the noble metals nanoparticles using two different reducing agents, ascorbic acid and sodium borohydride. The gold nanoparticles show an absorption band between 500nm and 550nm, silver nanoparticles show a band between 400 to 450 and the copper nanoparticle show the band between the 550nm to 600nm. Then, we interacts the silver and gold with three different antibiotics (cephalexin, ciprofloxacin and clindamycin). After the addition of the antibiotics to the colloidal silver and gold nanoparticles sample, we observed a change in absorption, a red shift and the creation of the new peak. The interaction of the antibiotics with Cu nanoparticles will be presented. Concentrations profiles are evaluated to establish the sensitivity and selectivity of the method.

COLL 353

Tuning activity of multi-metallic catalysts by designing and synthesizing model catalytic surfaces

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Catalysis plays a key role in the development of new processes for clean energy and sustainable chemistry. Specifically, the main challenge is to develop advanced catalysts with the merits of low-cost, high activity and selectivity, and durability used in many catalytic processes. To rationalize the search for high performance catalysts, our lab specializes in synthesizing model alloy systems with well-controlled surface compositions and surface structures. We extensively explored variety of key factors that impact the catalytic properties such as alloying effect, support effect, surface segregation, formation of surface phases and nanostructures, and roles of faceting planes, low coordinated sites. In this work, three electrocatalysts, *i.e.*, Au on Pd₃Fe(111), Pt ML on polycrystalline Hf-Ir and Pt ML on faceted C/Re(11-21) and O/W(111) nanotemplates, were prepared in vacuum, characterized using surface science techniques, and evaluated for their electrocatalytic activity for the oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), and ethanol oxidation reaction (EO).

COLL 354

Tailoring electronic properties of zinc oxide nanoparticles via the attachment of organic acid linkers

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Recently there has been much interest in the electronic and photonic properties of zinc oxide (ZnO) nanostructures as foreseeable applications include their use in solar cells. For such purposes, controlling surface functionalization is crucial and can be accomplished by the attachment of organic acids via the formation of self-assembled monolayers (SAMs). In this study, ZnO nanoparticles (<100 nm in size) were modified with organic SAMs containing phosphonic, hydroxamic, and sulfonic acid head groups. The modified nanoparticles were then characterized via infrared spectroscopy (IR), solid-state nuclear magnetic resonance spectroscopy (SS-NMR), powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM). UV-Vis absorption data was then used to determine the optical band gap of the systems, and cyclic voltammetry (CV) was used to determine the charge transfer effect of the samples. It was determined that both type of acid and concentration of acid have a noticeable impact on the properties of the ZnO.

COLL 355

Layer-by-Layer Silica Templated Assembly at the Nanoscale

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Templated assembly of silica onto nano- and micro-scale organic templates was achieved using a combination of chemical lift-off and aqueous solution chemistry performed under mild conditions of pH and temperature. Well-defined nanopatterns were created by electron beam lithography and used as templates for the generation of silica nanostructures. Initially, an amine-silane monolayer was vapor deposited onto the patterned substrates and subsequently reacted with silicic acid solutions made in buffers of varying pH and salt content at room temperature. The process of vapor treatment followed by the templated assembly of silica in aqueous solution could be repeated multiple times to perform layer-by-layer deposition while keeping the nanoscale organic templates intact. It was observed that the conditions for the silicic acid deposition, namely pH, salts and solution age, had a strong effect on thickness of each layer and the morphology of the amorphous silica formed.

COLL 356

Normal and 'Negative' Hysteresis Loops in Cyclic i-V Measurement Using Single Nanopipettes and Pumping Ions against Concentration Gradient

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We recently reported that the forward and backward current-potential curves cross at a non-zero cross-point in cyclic i-V measurements using single nanopipettes in ionic solutions. The cross-point separates a resistance-capacitance loop with normal phase shift from another one with negative phase shift. In this presentation, the transport behaviors of ions across a nanometer scale interface confined inside a single nanopipette are studied by steady-state and transient electroanalytical methods. A series of symmetric and asymmetric ionic concentrations inside and outside of the nanopipettes were employed. The nature of the nanoscale substrate-solution interface and its impact on the transport of ions against concentration gradient, the concept of ion pumping, will be discussed.

COLL 357

Fabrication of self-assembled template-based metal nanowires and metal nanoparticles using covalent bonding.

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The project involves fabrication of different nanoconjugates by self-assembling of metal nanowires (NW) and metal nanoparticles (NP) using covalent bonding as linkers. These nanoassemblies can be applied as building blocks in nano-electronic circuits. By attaching carboxylating agents to metal nanowires incorporated in a template, the carboxylic acid functionalities will be restricted to locate just on the tips of the metal

nanowires in a position-specific manner. Dissolving the template yields nanowires tagged with carboxylic acid groups. The formation of amide bond between the carboxylic acid modified nanowires and amine-modified nanoparticles is the driving force for creation of the nanoassemblies.

COLL 358

Synthesis of bimetallic silver-gold core-shell nanoparticles and their application to drug detection

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New methods for drugs detections are necessary to improve the time and sensitivity for drug testing. Our goal is the development of a simple strategy to produce bimetallic silver-gold core-shell nanoparticles for the study of drugs interactions. Formation of the NPs was achieved by the reduction of the AgNO_3 with NaBH_4 and HAuCl_4 with sodium citrate with polyethylene glycol. A conventional microwave was applied for complete the synthesis. This technology offers minimization of reaction times and stabilization of nanoparticles. In this research, we explore the interactions with Ultram and silver-gold core shell NPs. These nanoparticles show a peak centered around 523 nm. A new band formation centered in 230 nm was observed for the Ultram – core shell NPs performance. Characterization of the nanoparticles was performed using UV-Vis absorption spectroscopy and Transmission Electron Microscopy.

COLL 359

Reaction of hydrogen and organic peroxides with titanium impregnated films

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Reactions of gaseous hydrogen peroxide with titanium isopropoxide-hydroxypropylcellulose films prepared through sol-gel formation were investigated. The films were prepared with varied loadings of titanium isopropoxide on both glass and polycarbonate slides. When exposed to peroxide vapor the films changed from colorless to yellow. Higher titanium isopropoxide loadings displayed a more intense coloration over the course of exposure. In addition, the measured initial rates were dependent on the mass loadings, with films having higher titanium isopropoxide loadings showing more rapid colorization. However, films with the highest loadings displayed an increased tendency to crack and peel.

COLL 360

Use of Manganese ferrite (MnFe₂O₄) spinel nanoparticles as a alternative to remove nitrate in drinking water

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The concentration of nitrates in underground water has steadily increased over the last decades. As a result, this nitrate concentration has largely exceeded the required drinking water standards. Nitrates can block oxygen transport when ingested through water. Our work focuses in the application of manganese ferrite spinel nanoparticles (MnFe₂O₄) to remove nitrates from drinking water. This type of supermagnetic nanoparticle (SMP) has been used to remove contaminants in water, due to its electromagnetic properties. We successfully achieved the synthesis of the NPs by two different methods. Inverse micelle water/toluene system with polyvinyl alcohol as surfactant and low temperature combustion techniques using urea, glycine and glucose as fuels and chemical-precipitation method were performed. A black nanostructure powder was obtained using both methods. Both products show magnetic properties. Characterization of the nanoparticles was obtained using vibrating sampler magnetometer (VSM) and transmission electron microscopy (TEM).

COLL 361

Protein dynamics in ion-exchange chromatography

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Biologics such as recombinant proteins and monospecific monoclonal antibodies have become an important part of the pharmaceutical industry in recent years. The purification of biologics has presented new challenges due to their larger size and complexity compared to traditional small synthetic molecules. The most common purification method is ion-exchange chromatography. In our study we observed our protein alpha-lactalbumin using single molecule spectroscopy at both traditional, single charge adsorbents and at a unique cluster-charged adsorbent ion-exchange chromatography surface. This was done in order to discover the molecular mechanisms influencing protein interactions with different adsorbent structures. By analyzing association and dissociation data we have concluded that charge clusters not only increase the occurrence of specific interactions, but are in fact required for specific

interactions to occur between the protein and stationary phase. This presentation discusses the methods and conclusions behind this critically important result.

COLL 362

Video Microscopic Measurement of Static and Dynamic Surface Tension at High Temperatures

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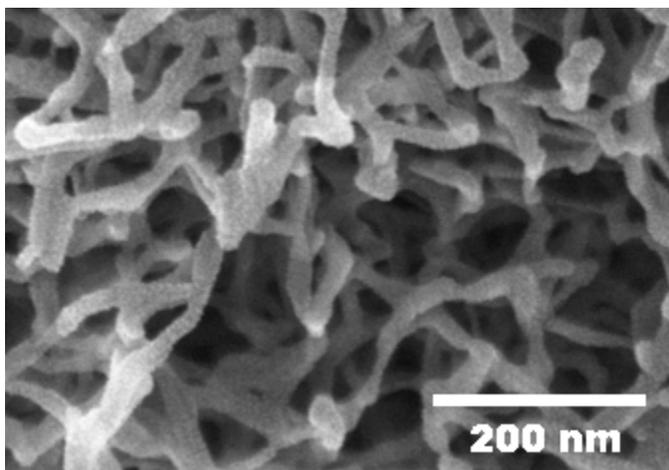
High-temperature measurements of static surface tensions by optical imaging of the liquid/gas interface inside a tapered micropipette which was placed within a microcapillary, were achieved by coating an electrically conductive, transparent, tin-doped indium oxide (ITO) thin film as a heating jacket on the outer surface of the microcapillary. The precision of this video microscopic technique was discussed by measuring static surface tensions of water, n-hexadecane, and n-decane at various temperatures, and the range achieved in the experiments was from 25 °C to 110 °C for n-decane and 25 °C to 200 °C for n-hexadecane. The experimental set up was further used for determining temperature-change induced dynamic surface tension, and for analyzing the effects of different factors on the dependence of surface tension on temperature and time.

COLL 363

Inexpensive synthesis of low-density nanofibrous vanadia monoliths from VOCl_3

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Nanoporous vanadia (VO_x) has applications in catalysis, Li intercalation, and low-density sacrificial energy absorption. The traditional method for synthesis of high-quality nanoporous VO_x aerogels is the controlled hydrolysis of expensive vanadium alkoxides. We present a synthetic method utilizing VOCl_3 that reduces the cost of VO_x aerogels by a factor of 10 while maintaining the nanomorphology of conventional methods. Vanadium nitride aerogels were formed via pyrolysis under NH_3 . The gels were characterized via SEM, TEM, XRD, XPS, UV-Vis, and Raman spectroscopy.



COLL 364

Bimetallic Copper-Gold Nanoclusters Protected with Mixed Dithiolate and Monothiol Ligands

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Bimetallic nanoalloys display novel properties and functions defined by the metal composition and the synergistic effects from the surface. The impacts of surface increase as the overall nanoalloy size decreases to a few nanometers or less, or novel surface bond structures emerge. Here in, we describe the synthesis of bimetallic nanoclusters composed of copper and gold cores stabilized by a mixed monolayer of dithiolate durene (Durene-DT) and monothiolate phenylethanethiol (PhC2S) ligands. Via the variation of synthetic conditions, unique Cu-Au nanoclusters are obtained. Discrete absorption bands and near infrared (IR) photoluminescence are observed in optical studies. Electrochemical measurements reveal the activities such as quantized double charging at lower potential window and Cu redox signals. The nanoclusters are characterized by ¹H NMR, mass spectroscopy, transmission electron microscopy and energy dispersive X-ray analysis, etc. Ongoing studies include further elucidation of the chemical composition and structures, especially the metal-thiolate interactions at the core-ligand interfaces.

COLL 365

Stability studies of P3HT:PCBM/electrode interfaces

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The polymer/electrode interface has crucial effects on the properties exhibited by organic devices, such as polymer-based photovoltaics (PPVs). One of the most researched material for PPVs is the P3HT:PCBM blend (poly(3-hexylthiophene:phenyl-C₆₁-butyric acid methyl ester). In this work, the stability of the interface formed between an electrode and the P3HT:PCBM blend has been studied by I-V measurements in nitrogen environment, thus eliminating the influence of oxygen and moisture. It was observed that when Al is used as an electrode, the dark I-V characteristic of the device changes slowly and stabilizes only after several hours. The results suggest diffusion of Al atoms into the active polymer layer. In the presence of an aluminum oxide layer, the device exhibited fairly stable dark I-V. As will be shown, the stability of the polymer/electrode interface significantly influences the resulting macroscopic properties, such as photoconducting properties and thermal annealing effects.

COLL 366

Crystallization of RDX on 2D Templates: Surface and Solvent Effects

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Hexahydro-1,3,5-trinitro-1,3,5-triazine (**RDX**) is a polymorphic secondary explosive which is commonly used in military and industrial applications. Though widely studied, a detailed understanding of how the crystal growth conditions affect the physical properties of this compound remains incomplete. Towards this goal, we have investigated the template-directed crystallization of RDX on 2D self-assembled monolayers (SAMs). Results show that the surface functionality and the growth solvent both play a significant role in determining the crystal morphology, nucleation density and surface orientation. Analysis of the intermolecular interactions occurring at different crystal/SAM interfaces as well as the material's growth rate anisotropy provides some insight into how heterogeneous nucleation and growth affects the material properties.

COLL 367

Hypoxia-Induced Disassembly and Active Tumor Targeting of LbL Nanoparticles

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Integrated polymer nanotechnologies provide exciting new opportunities for multicomponent drug delivery to solid tumors. These strategies can maximize tumor-specific drug delivery and provide both spatial and temporal control over the release of compounds, leveraging optimal therapeutic synergy and minimizing off-target effects.

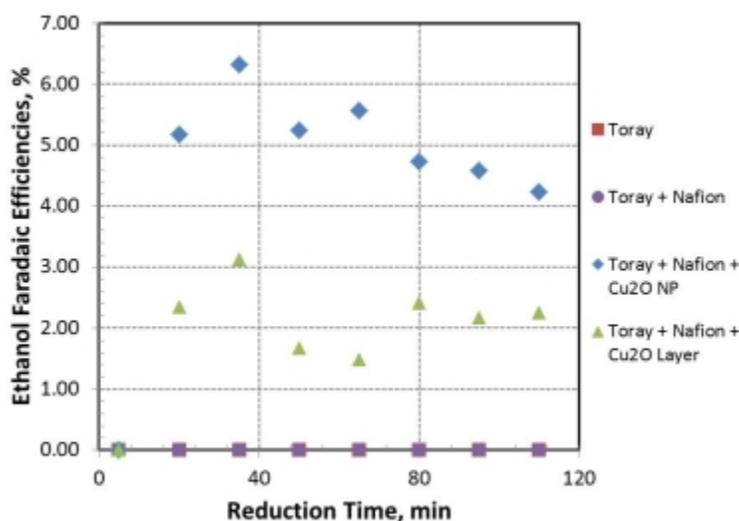
Koch Institute researchers in the Hammond Lab are developing modular nanotechnology platforms for combinatorial RNA interference and cancer chemotherapy that incorporate colloidal drug carriers and multifunctional layer-by-layer (LbL) polymer assemblies. These constructs allow for the inhibition of currently un-druggable targets and recapitulate the optimal sequencing and timing of drug combinations screened in vitro. Herein, we present recent progress in engineering tumor-targeting stealth polymer multilayer components for these novel particle technologies that disassemble at hypoxic tumor pH. These multifunctional LbL components both stabilize and block non-specific adsorption, bind cell surface adhesion receptors associated with drug-resistant, tumor-initiating, and drug-resistant cellular phenotypes, and selectively erode at hypoxic tumor pH.

COLL 368

Kinetics of ethanol formation from carbon dioxide using supported copper oxide electrocatalyst

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The kinetics of electrochemical conversion of carbon dioxide to ethanol at a constant applied potential of -1.7 (Ag/AgCl) was demonstrated in two types of supported copper (I) oxide catalyst; namely (1) Cu_2O nanoparticles pasted onto a Toray carbon fiber paper by a nafion binder, (2) electrochemically deposited Cu_2O layer on a nafion-coated Toray carbon fiber paper. GC-FID measurements reported average formation rates of 2.5 ± 0.2 and $0.9 \pm 0.2 \mu\text{mol}/\text{cm}^2\cdot\text{hr}$ with faradaic efficiencies of 5.1 ± 0.7 and 2.2 ± 0.5 % respectively for $t = 110$ minutes.



COLL 369

Green-synthesis of silver nanoparticles with *Artemisia capillaris* extracts

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By using a green-synthetic approach, we used both water and 70% ethanol extracts of *Artemisia capillaris* as a reducing agent for generating silver nanoparticles (AgNPs). The formation of AgNPs was confirmed by using UV-Vis spectrophotometry, Fourier transform infrared spectroscopy, high resolution-transmission electron microscopy and atomic force microscopy. The average diameter was 29.71 nm with the water extract and 29.62 nm with the 70% ethanol extract. AgNPs exerted a significant enhancement of antibacterial activity against five strains (*Pseudomonas aeruginosa*, *Escherichia coli*, *Enterobacter cloacae*, *Klebsiella oxytoca*, and *Klebsiella areogenes*) when compared with the extract alone. AgNPs generated by the 70% ethanol extract showed slightly higher antibacterial activity than those produced with the water extract. These results suggest that plant extracts have the potential in being powerful reducing agents for the production of biocompatible AgNPs with enhanced antibacterial activities.

COLL 370

Enhanced anticoagulant activity with heparin-reduced gold nanoparticles

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Heparin is an acidic polysaccharide currently used as an intravenous anticoagulant drug. In this report, heparin was used as a reducing agent for the green-synthesis of gold nanoparticles (AuNPs). Its nanotopography was extensively studied with atomic force microscopy. The newly prepared AuNPs with mostly spherical and amorphous shapes showed its characteristic surface plasmon resonance bands at 525-528 nm. The average diameter measured to be either 20.26 ± 3.35 nm or 40.85 ± 8.95 nm, depending on the precursor salt and heparin concentrations in the reaction mixture. The evaluation of the anticoagulant activity of heparin-reduced AuNPs exhibited prolonged prothrombin time (26.7% increase), thrombin time (21.8% increase), and activated partial thromboplastin time (23.2% increase) compared with the control heparin. Therefore, the combination of two materials, heparin and AuNPs, produces a synergistic effect on anticoagulant activity demonstrating the possible applications in the area of nanomedicine and nanobiotechnology.

COLL 371

Hydrophobic recovery of polydimethylsiloxane surfaces after oxygen plasma treatment

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Oxygen plasma treatment is commonly used to impart hydrophilicity to inherently hydrophobic polydimethylsiloxane (PDMS). However, the effect of plasma treatment on PDMS prepared from the commercial kit, Sylgard 184, is short-lived as hydrophobic recovery is observed within hours. The rapid hydrophobic recovery is attributed to the migration of low molecular weight (LMW) species to the surface. The effect of LMW species was investigated by deliberately adding them to a simplified PDMS system fabricated using hydrosilylation of vinyl and -SiH functionalized PDMS prepolymers. Long exposure to high vacuum was also evaluated as a method to remove LMW species and to slow down recovery. After short vacuum exposure, the rate of recovery was proportional to the percentage of LMW species added and inversely proportional to the molecular weight of the species. After extended vacuum exposure, these trends were eliminated and hydrophobic recovery of all PDMS systems including Sylgard 184 was substantially reduced.

COLL 372

Surface-modified gold nanorods for self-assembly

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Hybrid organic-gold nanostructures couple the functionality and synthetic flexibility of organics with the plasmonic properties of metallic nanoparticles. Gold nanorods (AuNRs), due to their inherent anisotropy, feature highly tunable optical properties and selective surface modification at the longitudinal or transverse axes. These attributes lead to fascinating self-assembly phenomena and can be exploited to design photothermal materials triggered by tunable wavelengths. In this research, we capped AuNRs with a variety of organic species, including 'clickable' azide moieties and hyperbranched polymers capable of hosting small molecules. With this diverse library, we investigated the partitioning of the modified AuNRs into novel vesicles. This research advances the development of plasmonic, stimuli-sensitive materials.

COLL 373

Ultrafast Thermal Analysis of Surface Functionalized Gold Nanorods in Aqueous Solution

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The thermal transport properties of surface-functionalized gold nanorods in aqueous solution are investigated with transient absorption, following femtosecond pumping of the longitudinal localized surface plasmons. The thermal conductivities and heat capacities of surfactant and polymer coating layers are extracted from transient absorption; thicknesses of the layers are measured by dynamic light scattering. The rate of change of the absorption of gold nanorods in aqueous solution varies with the probe laser wavelength due to the shift in the plasmon resonance created by heating of media surrounding the particles. The measurements of the cooling dynamics of gold nanorods are optimized by pumping and probing at the absorption peak of the sample. The heat capacity of the surfactant cetyltrimethylammonium bromide (CTAB) layer is $\sim 2.0 \text{ J cm}^{-3} \text{ K}^{-1}$; the thermal conductivity of the CTAB layer drops from $0.24 \text{ W m}^{-1} \text{ K}^{-1}$ to $0.18 \text{ W m}^{-1} \text{ K}^{-1}$ at solution concentrations above the CTAB critical micelle concentration. Layer-by-layer polyelectrolyte coatings using poly(acrylic acid) (PAA) and polyallyamine hydrochloride (PAH) increase the thermal conductivity and heat capacity of the surface layer; greater water penetration into PAH-terminated surface layers have increased the thickness, thermal conductivity, and heat capacity relative to PAA-terminated layers.

COLL 374

A Novel Gel Completely Composed of Salts

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Room temperature molten salts, or ionic liquids (ILs), are novel materials that have received heightened attention due to their unique molecular nature and wide range of applications. They are salts with irregularly shaped ions that resist crystalline packing and thus remain liquid at room temperature. Herein we describe the spontaneous gelation of a binary mixture of ionic liquids in the absence of any additional gelator molecules. The two ILs are mutually miscible (although inter-diffusion is slow) up to a certain point, at which the system forms a viscoelastic gel. Using confocal laser scanning microscopy, we describe the gelation process on a microscopic level with emphasis on the self-assembled fiber morphologies. Furthermore, we also provide rheological and thermophysical properties on this unique gel. This unique system has potential applications in batteries, coatings, lubricants, etc.

COLL 375

Investigation of Salt-Surfactant Mesophases and Its Application of Materials Synthesis

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Formation of Lil-non-ionic surfactant (10-lauryl ether, C₁₂EO₁₀ and Pluronics) lyotropic liquid crystalline (LLC) mesophases with and without I₂ and incorporation of Lil/I₂ couple into LiCl-non-ionic surfactant LLC mesophases have been investigated using XRD, POM, DSC, UV-vis absorption, FTIR, Raman, and conductivity measurement techniques. Lil can be directly assembled into LLC mesophases in the presence of a minimum amount of water. I₂ can be incorporated into the LLC phase without disturbing the mesophase up to 0.2 mole ratio for Lil-C₁₂EO₁₀ and LiCl-C₁₂EO₁₀. Like in many solvents, some I⁻ can be converted into I₃⁻ ion that its concentration can be increased by the addition of I₂ into the LLC media. The XRD patterns and POM images clearly showed that the above mixtures form stable LLC mesophases in a very broad salt concentration. Overall the Lil and LiCl-Lil with and without I₂ and non-ionic surfactants form stable LLC mesophases with high ionic conductivities.

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COLL 376

Preparation and subsequent surface PEGylation of crosslinked poly(dimethylsiloxane) substrates with tunable moduli

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Mechanical patterns on cell culture substrates can be potentially used as effective cues in directing cell migration. Fully functional substrates require not only readily tunable modulus but also proper surface properties to ensure proper interactions with the surrounding media. In this study, crosslinked poly(dimethylsiloxane) (PDMS) with tunable modulus ranging from 50 to 1000 kPa was fabricated using platinum-catalyzed

hydrosilylation from vinyl and -SiH functionalized prepolymers. To overcome hydrophobicity of the PDMS surface, vinyl-terminated poly(ethylene glycol) (v-PEG) was grafted onto crosslinked PDMS thin films containing excess -SiH functionality via surface hydrosilylation reaction. Efficiency of surface PEGylation is controlled by surface density of -SiH groups, molecular weight of v-PEG, and catalyst concentration.

COLL 377

Optical Properties of encapsulated squaraine dyes in aqueous solutions

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Due to the strong absorption and emission properties which respond to the surrounding medium, squaraine dyes have been receiving significant attention as a potential candidate of photosensitizers for photodynamic therapy (PDT) applications. Therefore, squaraine dyes have been extensively investigated in recent years, from both fundamental and technological viewpoints. We Encapsulation of squaraine dyes with amylose, and conformational transitions of amylose upon complexation with the dyes were investigated using UV-visible, fluorescence, and circular dichroism (CD) spectra and two-photon absorption properties in various DMSO/H₂O mixtures.

COLL 378

Functionalized Colloidal Supported Metal Nanoparticles (CSMNs) as Efficient Recyclable Nanocatalysts for Liquid-Phase Heck Reaction

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Transition metal nanoparticles show excellent catalytic activity because of their small size. We investigate the catalytic activity, stability and recycling potential of two different types of nanocatalysts. The two types of catalysts used are the palladium nanoparticles supported onto the surface of functionalized and unfunctionalized silica colloids. We used aminopropyltriethoxysilane (APTES) as the linker to functionalize silica colloids. These catalysts are used to catalyze Heck-reaction between styrene and iodobenzene that forms *trans*-stilbene. The fresh and recycled catalysts are characterized using TEM and EDS to observe any changes that might be taking place to the catalysts after its use in the reaction. Our studies showed that the palladium nanoparticles supported onto unfunctionalized silica colloid supports showed more catalytic activity compared to the

palladium nanoparticles supported onto functionalized silica colloid supports after the first cycle of Heck-reaction. However, the palladium nanoparticles supported onto functionalized silica colloid supports showed more stability and recycling potential compared to palladium nanoparticles supported onto unfunctionalized silica colloid supports.

COLL 379

Hierarchical surface patterning by wettability controlled nanoparticle transfer from wrinkled surfaces

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Assemblies of nanoparticles are promising building blocks for future lab-on-a-chip devices such as sensors. Recently, ordered arrays of nanoparticles have been realized by convective assembly on surface-wrinkled elastomers. While this simple and lithography-free procedure is compatible with a variety of functional particles, technological applications require a transfer of the formed colloidal assemblies onto flat solid substrates. We present a new method in which colloidal assemblies are transferred by capillary forces. In contrast to classical “lift-off and transfer” methods, conformal contact between the particles and the target substrate is not required. However, successful particle transfer depends on the wettability of the target substrate and can be suppressed by a hydrophobic monolayer. By chemical surface patterning locally controlled particle transfer is possible with high precision. Our method is robust enough to conduct multiple colloid deposition steps, resulting in hierarchical structures that could find application in plasmonic sensing or the construction of metamaterials.

COLL 380

Partial Molar Volume Measurements of Water Molecular Interactions in AOT Reverse Micelles

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Partial molar volume measurements are used to investigate how water molecular structure and interactions varies in nanoconfined spaces. The experiments are performed in AOT reverse micelles wherein the size of the water droplet and the relative proportion of interfacial water can be easily controlled by the simple formulation ratio w_0 . Partial molar volume measurements of water in reverse micelles are relatively few; however, some have suggested novel structural changes in the liquid water domain occurring at w_0 values in the 9-13 range. [*Langmuir* **2000**, 16, 3633-3635] Because this observation does not correlate well with other determinations of water properties in AOT

reverse micelles, our research will investigate these changes using three different approaches to measuring partial molar volume: via a technique we are developing that uses dynamic light scattering measurements of reverse micelle diameter, via bulk density measurements, and also via traditional solution methods. Experiments are performed over a range of reverse micelle size in order to assess the effect of nano-confinement on water interactions.

COLL 381

DFT Studies of How Particle History and Bonding Competition Effect Reactivity in Model Rutile TiO₂-Water Interfaces

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The water vapor present under environmental and operation conditions transforms the exposed surfaces of solid oxides into reactive oxide-metal interfaces with stoichiometries and functional groups different from those found under ultra-high vacuum conditions. Here, the interaction of gas-phase CO₂ and SO₂ with hydroxylated TiO₂ surfaces is studied using DFT-based modeling. Our goal is to address fundamental questions of oxide-water interface reactivity, as well as to aid in explaining literature experimental studies that report distinct reactivity of surface hydroxyl groups towards the two triatomic species. Using atomistic thermodynamics, we explore how the preparation or history of TiO₂ may influence surface structure and, importantly, surface functional group identity, under ambient conditions. We model CO₂ and SO₂ adsorption at various surface functional groups, and also consider additional proton rearrangement between surface hydroxyl groups and adsorbates. We report adsorption energies, details of atomic and electronic structure, vibrational frequency analysis, and details of electronic structure. From our results we suggest which surface reaction mechanisms give rise to the most stable adsorption products.

COLL 382

Rapid contents release from QPA-DOPE containing vesicles as a result of a reduction-induced phase transition

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The potential is great for liposome drug delivery systems that provide specific contents release at diseased tissue sites upon activation by upregulated enzymes; however, this potential will only come to fruition with mechanistic knowledge of the contents release process. NAD(P)H:quinone oxidoreductase type 1 (NQO1) is a target for reductively-responsive liposomes, as it is an enzyme upregulated in numerous cancer tissues and is capable of reducing quinone propionic acid (QPA) trigger groups to hydroquinones that self cleave from dioleoylphosphatidylethanolamine (DOPE) liposome surfaces,

thereby initiating contents release. Here we report that the observed contents release is associated with a lamellar to inverted hexagonal phase transition ($L_{\alpha} \rightarrow H_{II}$), based on ^{31}P NMR lineshapes for QPA-DOPE giant unilamellar vesicles (GUVs) before and after chemical reductive activation. Furthermore, the rate of contents release is rapidly accelerated due to the presence of increasing amounts of palmitoyl-oleoyl phosphatidylethanolamine (POPE) in large unilamellar vesicles (LUVs).

COLL 383

Tortuosity of nanoporous hosts determines the into which polymorph confined pharmaceuticals crystallize

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We show that the polymorph into which acetaminophen confined to nanoporous hosts crystallizes can be determined by the tortuosity of the nanopore system. If crystal growth rather than nucleation dominates crystallization and parent crystals growing into the pores are available, uniformly oriented form II crystals form in the straight cylindrical pores of anodic alumina (AAO). Under otherwise identical crystallization conditions, more stable forms I or III predominantly grow in controlled porous glasses (CPGs) with continuous, spongelike pore systems. Fast-growing crystals in CPGs impinge on the pore walls after growth paths of a few 10 nm and occupy only a negligible volume fraction. These results shed light on the mechanism underlying oriented crystallization in two-dimensional confinement, which was reported for a broad range of functional materials, and should have significant impact on the mesoscopic design of drug delivery systems as well as on other areas such as nanowire-based organic electronics.

COLL 384

Adsorption of poly(vinyl alcohol) onto gold nanoparticles from dilute aqueous solution

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Stabilization of Gold nanoparticles (AuNPs) to prevent them from aggregation is important to ensure their unique electronic and optical properties. Citrate reduced AuNPs are stabilized by the absorbed citrate moieties. The electrostatics repulsion, however, is lost under low pH and/or high ionic strength conditions. In this research, poly(vinyl alcohol) (PVOH), a neutral and water-soluble polymer, was adsorbed onto AuNPs to impart nanoparticle stabilization in solution. This study focused on the effects

of AuNP size and PVOH molecular weight and degree of hydrolysis on adsorption. Dynamic light scattering was used to measure hydrodynamic diameters of AuNPs, PVOH chains, and their conjugates. Langmuir adsorption isotherms were constructed to characterize binding constant and maximum polymer adsorbed. Binding constant depends strongly on PVOH degree of hydrolysis and the maximum amount adsorbed is mainly a function of PVOH molecular weight. The conformation of AuNP-PVOH conjugates depends on the relative sizes of AuNPs and PVOH chains.

COLL 385

Structural characterization of soy protein nanoparticle aggregates from high shear microfluidization

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Soy protein nanoparticles were produced with a microfluidizer and characterized in terms of particle size, size distribution, morphology, rheological properties, and aggregate structure. Three stages of structure breakdown were observed when the soy protein dispersion was passed through the microfluidizer. A sudden change in the aggregate size was observed after a certain number of passes through the microfluidizer; such change was both concentration and pH dependent. Rheological measurements of these soy protein emulsions showed that both viscosity and storage/loss modulus decreased as the aggregate size of soy protein was decreased, indicating reduced interactions between the aggregates. The fractal dimension of the soy protein aggregates was estimated from the properties of a continuous matrix embedded with the aggregates.

COLL 386

Chemical immobilization of bone morphogenetic protein 2 on ceramic scaffolding enhances substrate bioactivity

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Bone morphogenetic protein 2 (BMP-2) is a member of the TGF- β growth factor family that exhibits multiple functionalities in the process of bone remodeling. As such, surface modification of intrinsically bioactive ceramic scaffolds with BMP-2 could serve to further enhance the osteogenic effects of the scaffolds at a bone defect site. In this study, calcium aluminate and calcium phosphate scaffolds were modified with BMP-2 by direct surface adsorption or chemical immobilization utilizing an organic linker system. The effect of surface modification was evaluated by human osteoblast growth at Days 1, 4, and 7 using a Live/Dead Cytotoxicity assay. Differentiation of adult mesenchymal stem cells was evaluated on the substrates using an alkaline phosphatase assay. It was shown that the method of biomolecule attachment as well as scaffold composition

influenced cell viability and differentiation and that chemically immobilized BMP-2 on CaP scaffolds promoted cell viability to the highest degree.

COLL 387

Gold Nanoparticle-Induced Cell Death: Solid Gold Nanospheres versus Hollow Gold Nanocages

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Recently, we have shown that targeting the cancer cell nucleus with solid gold nanospheres, using a cancer cell penetrating/pro-apoptotic peptide (RGD) and a nuclear localization sequence peptide (NLS), inhibits cell division, thus leading to apoptosis. In the present work, we report the use of peptide-conjugated solid gold nanospheres and hollow gold nanocages to induce cell death in cancer cells. Gold nanocages were found to exhibit an enhancement in terms of, cell cycle changes, reduction of ATP, generation of reactive oxygen species (ROS), and, most important, the ability to induce apoptosis and necrosis. This evidence suggests that the presence of silver oxide (*i.e.* oxidized metallic silver) on the inner cavity of the hollow cage causes ROS generation and thereby induces greater cell death than the solid spheres. Another suggested cause is the packing of ligands on the surface of the cage, namely the pro-apoptotic RGD peptide, which would render an extended conformation of ligands on the surface of the cage, thereby enhancing their biochemical activity. Overall, the results here have important implications in understanding the interactions between nanomaterials and living systems and provide new information based on not only the metallic composition, but the shape of the nanocomposite.

COLL 388

Surface enhanced fluorescence using silica-coated gold nanorods

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Gold nanorods are rod-shaped nanoparticles with unique optical properties. The collective oscillation of surface electrons (called plasmons) causes electromagnetic field enhancement near a gold nanorod surface. Recently, researchers have exploited this property to achieve increased excitation rates and emission from fluorescent dyes when they are near gold nanorods. This phenomenon, known as surface-enhanced fluorescence, is distance dependent. When a dye molecule is too far away, the strength of the electromagnetic field is reduced and when a dye molecule is too close to a plasmonic surface there is non-radiative energy transfer and fluorescence quenching

occurs.

Herein, we investigated the distance dependent fluorescence of a series of fluorescent dyes put at a fixed distance from gold nanorods. Gold nanorods having aspect ratios 1 – 4 were synthesized using the well-known method developed by Murphy and El-Sayed. Distance dependence was achieved by coating gold nanorods with a dielectric silica shell that was varied between 10 and 40 nm using a modified Stöber method. The dye molecules were then loaded onto the silica surface through electrostatic or covalent interactions. Fluorescence excitation and emission were measured to determine how distance from the gold nanorod surface affected fluorescence behavior. We find that the wavelengths of dye excitation and emission as well as the silica shell thickness can affect fluorescence behavior.

COLL 389

Controlling temperature and light response of layer-by-layer assemblies of hybrid nanoparticles grafted with responsive diblock copolymer brushes

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We report on synthesis and layer-by-layer (LbL) assembly of hybrid nanoparticles (hNPs) composed of gold nanoparticles (Au NPs) grafted with dually stimuli-responsive diblock copolymer brushes. hNPs with varied block lengths were prepared by surface-initiated atom transfer radical polymerization (SI-ATRP) of N-isopropylacrylamide (NIPAM) and sodium methacrylate (NaMA). The brush grafting density, polymer molecular weights and block lengths of grafted polymers were determined by a combination of thermogravimetric analysis (TGA) of hNPs, and nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) of poly(N-isopropylacrylamide)-*block*-poly(methacrylic acid) (PNIPAM-*b*-PMAA) cleaved from Au NPs. In solution, hNPs demonstrated swelling that was strongly dependent on solution pH and temperature. LbL assembly of hNPs with branched polyethyleneimine (BPEI) resulted in robust films stable in a wide range of pH values. Importantly, temperature and light response of these films could be controlled by PNIPAM's block length of grafted polymers.

COLL 390

Pronounced Effects of Anisotropy on Plasmonic Properties of Nanorings Fabricated by Electron Beam Lithography

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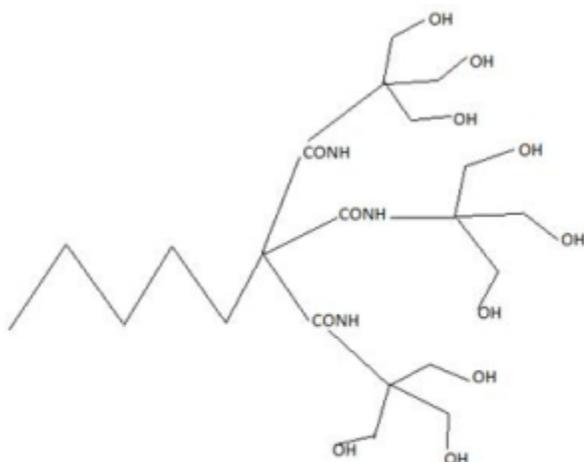
Gold nanoring dimers were fabricated via Electron Beam Lithography. The coupling between the inner and outer surfaces of a single nanoring renders it very sensitive to any anisotropy. The nanorings demonstrate exceptional sensitivity to asymmetries in particle shape and high index substrate effects. This results in a Fano lineshape for the dipolar plasmon resonance bands. The traditional file preparation methods for theoretical modeling are unable to accurately represent this slight anisotropy. Accordingly, a method was developed for preparing the files describing the nanoparticle shape for theoretical calculations wherein an SEM image of the particle(s) is directly used to create the file. This method is easy to execute and should therefore become the new paradigm for particle shape descriptions in future calculations. The improved sensitivity of these nanorings due to their geometry and increased field enhancement in the cavity make them attractive for absorption or fluorescence enhancement applications in the future.

COLL 391

Micellar assembly and dynamics of one-Directional arborols

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One-directional [9]-6 arborols are half-dumbbell-shaped dendrimers which possess a large hydrophilic head consisting of nine hydroxyl groups ([9]-), and a hydrophobic moiety composed of a 6-carbon alkyl chain. In a previous report,¹ the critical micelle concentration (CMC) of these molecules was determined (8.8 mM). See Figure 1 for the molecular structure of a single [9]-6 arborol. Dynamic light scattering was used to determine the diffusion coefficient of [9]-6 self-assembly at various concentrations, above and below the CMC. The hydrodynamic radii of the micelles were plotted as a function of concentration to gain insight about the micellar structural properties.



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COLL 392

Synthesis and characterization of biocompatible Gadolinium Oxide nanoparticle MRI contrast agent

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In this work Gadolinium oxide (Gd_2O_3) nanoparticles, as potential MRI contrast agents, were synthesized in a broad range of diameters through high temperature thermal decomposition method. Characterization was carried out by Transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The biocompatible hydrated Gd_2O_3 nanoparticles formed in the next step using Polyethylene glycol (PEG) as surface coating, which were shown stable over long time, based on Dynamic Light Scattering (DLS) data. High longitudinal relaxivity (r_1) of biocompatible PEG coated Gd_2O_3 nanoparticles were obtained by optimizing their core diameter and PEG average molecular weight. We observed no significant toxicity of PEG coated Gd_2O_3 on human dermal fibroblasts (HDF) according to in vitro cell toxicological studies. Based on the result of this work, our biocompatible Gadolinium Oxide nanoparticles have the potential to be promising MRI contrast agents due to their high r_1 value and low toxicity.

COLL 393

Formation of Conducting Networks by Liquid-Bridging in Colloidal Self-Assemblies

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Recently, conductive networks have attracted much attention for potential use in microelectronics and nanophotonics. For practical applications, it is important to develop a simple and reliable method of fabricating conductive networks. There have been several approaches to the construction of such networks, for example, photolithography for metal inter-connection, ink-jet printing using silver ink. However, these methods limit the feature resolution on a micrometer scale and uniformity over large area.

Here, we present a powerful way of producing conductive networks by liquid bridging in self-assembly of colloidal particles. Since the capillary force is generated between the close-packed colloidal particles, the assembly can be used as a template for a conducting material in the liquid state. Through the liquid-bridging phenomenon, the conducting networks of the order of submicrometer can be spontaneously formed depending on the spin-coating rate. Our approach is expected to play a critical role in developing diverse electronic and optoelectronic devices.

COLL 394

Behaviors of quinoxaline dendrimers at the air-water interface

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Molecular conformation and orientation of 2,3-bis(4-(2,3-bis(4-methoxyphenyl)quinoxalin-6-yloxy)phenyl)quinoxaline-6-carboxylic acid ([G2-DPQ]-CO₂H: G2) and 2,3-bis(4-(2,3-bis(4-(2,3-bis(4-methoxyphenyl)quinoxalin-6-yloxy)phenyl)quinoxalin-6-yloxy)phenyl)quinoxaline-6-carboxylic acid ([G3-DPQ]-CO₂H: G3) at the air-water interface have been investigated using surface pressure-area isotherms by Langmuir-Blodgett technique, Atomic Force Microscopy, UV-vis spectroscopy, and X-ray reflectivity.

In the case of G2, the surface pressure-surface area isotherm shows a steep increase around 100 Å²/molecule. G2 experiences a direct transition from the gaseous phase to the solid phase, and molecules are compressed without complicated transitions. The monolayer of G2 is aligned straightly at 5 mN/m. At higher surface pressure near 20 mN/m, G2 molecules maintain their ordering and form a close-packed arrangement.

In contrast to G2, the isotherm for G3 shows a gradual increase owing to the flexibility of G3 molecules. G3 molecules form circular domains at the surface pressure of 1 mN/m as a result of the difference in hydrophobicity between the core group and the peripheral end group. Upon further compression, G3 made many aggregate domains, size of ~ 40 nm.

COLL 395

Synthesis of Magnetic Catalyst with Multiple Core-shell structure and Its High Activity for Styrene Epoxidation

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Fe₃O₄/CuO/mesoporous silica (mSiO₂), a novel magnetic catalyst with multiple core-shell structure was successfully fabricated. The Fe₃O₄ core was modified with polyacrylic acid (PAA) via a simple one-step solvothermal method. The carboxylate groups of PAA had a strong coordination with copper cations, which promoted the efficient load of CuO. The outer mesoporous silica shell not only provides catalytic reaction channels, but also develops a strong protect layer to avoid the loss of active CuO. The as-synthesized Fe₃O₄/CuO/mSiO₂ can catalyze styrene epoxidation, in which the conversion of styrene is almost 100% and the selectivity of styrene oxide is more than 90%. The results are better than the reported ones. The catalyst can be separated from the reaction system quickly under magnetic field, and re-used for further at least 10 runs without obvious decrease of efficiency. We thank the National Natural Science Foundation of China (Grant No. 50836001 and No. 51272028) for support.

COLL 396

Amphiphilic Structure-Surface Property Relationships of Monosaccharide-Based Surfactants

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A set of monosaccharide-based renewable surfactants has been prepared, structurally checked, and systematically screened for different activities and functionalities. These compounds vary in the polar headgroup, linker, and hydrophobic tail. Beyond the goal to find out the most potential valuable surfactants for each measurement, relationships between chemical structure, basic properties, and functionalities have been examined by comparing compounds differing in a single structural variable. In this paper, we show and explain the impact of the anomeric alpha or bêta, neutral or acid sugar derivatives,

equatorial or axial position of hydroxyl group, alkyl chain substitute attachment position, number, and length on surface properties of sugar-based surfactants.

COLL 397

Enhanced fluorescence of nano-sized colloids for the targeted immunofluorescence labeling

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Fluorescence labeling is a very useful analytical technique for investigating the structure of live cells. Inorganic quantum dots or organic fluorescent dyes have been used in the immunofluorescence labeling due to their high quantum yield, high molar extinction coefficients, broad absorption with narrow light emission, and good photo physical and chemical stability. But, the semi-conducting quantum dots are toxic for any living cell and self-quenching of organ fluorescent molecules is critical for a steady imaging. Thus, developing highly emissive, biocompatible, and chemically readily modifiable luminescent materials is strongly desired. Here, we report the enhanced photoluminescence of nano-sized colloids with heterocyclic organic compounds for possible use in the field of immunofluorescence labeling.

COLL 398

Nitric Oxide (NO) release from self-assembled monolayers

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Nitric oxide (NO) is a molecule that has significant biological consequences. It is involved in signaling pathways, acts as a vasodilator, and can cause dispersal of biofilms in the human body. This project was designed to create a nitric oxide (NO) releasing film that was responsive at biological conditions. Previous research has shown that S-nitroso-N-acetyl-D,L-penicillamine (SNAP) liberates NO at biological temperatures (37 °C) but is stable at room temperature. Here, SNAP was immobilized on a substrate (stainless steel 316L) using a self-assembled monolayer of 12-aminododecanoic acid. First, the amine terminus of the monolayer was functionalized with N-acetyl-L-penicillamine (NAP). Then, the thiol group of the NAP was converted to a thionitrite group yielding an even monolayer of SNAP on a model substrate. Reactions were analyzed by surface infrared spectroscopy and MALDI-TOF MS.

COLL 399

Preparation and evaluation of biocompatible surface using Perhydropolisilazane

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Perhydropolysilazane (PZ) is known to convert into high-density silica by simply heating in the presence of adequate oxygen and water. We have recently verified that PZ can be employed as a material to prepare functional surface by simply attaching the functional compound with hydroxyl group, on the time PZ was heated to produce silica film. In this study, several compounds with hydroxyl group, such as ethylene glycol oligomer (EGO) and its derivatives were attempted to immobilize on the surface of substrate using PZ. Platelet-Rich-Plasma adsorption test was performed for biocompatibility evaluation. The biocompatibility of the substrate was improved by the immobilization of EGO.

COLL 400

Effect of the Ligand Position on the Supramolecular Interactions between Self-assembling Dendrimers and Proteins

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The molecular design of biaryl amphiphilic self-assembling dendrimers allow for location of a ligand at a singular position of the molecule. The possibilities increase according to dendrimer generation. The assembled micelle-like nanostructures can encapsulate small fluorescent molecules in their hydrophobic interiors, which can be released by disruption in the nanostructure Hydrophilic Lipophilic Balance. Attaching the ligand biotin at different layers of G1 and G2 dendrimers generated significantly different release profiles of the guest molecules, when the micellar disassembly was triggered by binding to the protein avidin. Different proteins with diverse sizes and PI did not trigger the disassembly and release beyond non-specific interactions. Disassembly and release were followed by DLS and fluorimetry. Having the ligand at the periphery of the dendrimers produced release of up to 70% of the dye Nile Red, showing that this location is the most favorable when a protein triggered release is desired, for both generations.

COLL 401

Assessing the surfactant critical aggregation concentration and diffusivity in crosslinked hydrogels

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Surfactant–polymer–drug interactions are highly dependent on the surfactant concentration and transport properties of polymeric hydrogels can vary drastically at and above the critical aggregation concentration (CAC) of the surfactant. It's important to estimate the CAC in order to design and tune hydrogels for drug release. The systems under consideration are the Brij surfactants and poly-hydroxyethyl methacrylate hydrogels. Here three methods to estimate CAC are discussed. The first method is based on changes caused in surfactant release due breakdown of aggregates. The second method relies on the effect of formation of the surfactant aggregates leading to a slowdown of a hydrophobic solute transport due to solute partitioning into the aggregates. The third method utilizes the fact that the water content of the gels increase with increasing surfactant amount. However the rate of increase will likely be discontinuous at the CAC. Surfactant diffusivity has also been estimated.

COLL 402

Switching of nanoparticle clusters and superlattices with pH-regulated DNA i-motif

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Self-assembly of nanoparticles driven by DNA hybridizations is a effective way for construction of nanoclusters and three-dimensional superlattices. However, such systems are typically static. We extend DNA-assembly methodology for fabrication of dynamically responsive and switchable nano-systems using i-motif DNA sequence, which confirmations are sensitive to pH value of the environment. We developed a simple yet effective approach for the switching the morphology of gold nanoparticle clusters between dimer and trimer structures by changing the pH value. Our experiments demonstrate that such cluster switching can be reliably cycled multiple times. Moreover, by employing both gold NP and fluorescent quantum dots, we show that cluster switching results in the pH-regulated optical response of the system. We also successfully fabricated three-dimensional superlattices using i-motif sequence as a linker. Our in-situ synchrotron-based small angle x-ray scattering measurements reveal repeatable lattice transformations during pH cycling and successful realization of this strategy for more complex DNA motifs.

COLL 403

Solvent-modulated amphiphilic block copolymer self-assembly into micelles and lyotropic liquid crystals

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Amphiphilic block copolymers of the poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) family are well-known for self-assembling in water (selective solvent for PEO) into (core-shell spherical) micelles, and, at higher concentrations, into cubic, hexagonal, and lamellar lyotropic liquid crystals. We are interested on how the aqueous phase behavior and structure of these polymeric amphiphiles can be modulated by the addition of polar organic solvents (e.g., glycerol, ethanol, propylene carbonate, triacetin) [1,2]. Mixtures of water with two organic solvents constitute a specific focus of this work [3,4]. Our studies aim to relate (i) the type of structure formed and its characteristic dimensions to the relative swelling of the polymer blocks and the solvent location in the amphiphile assembly, and (ii) the solvent effects to solvent properties. Solvent-induced structural changes have interesting repercussions in formulations and nanomaterials synthesis.

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COLL 404

Molecular Ordering in PCBM Monolayer Films on Ag and Au (111): From μ -aerosol deposited glasses to hcp packing

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Functionalized C₆₀ and C₇₀ fullerenes are increasingly employed as active components in organic electronic devices. The structure of the PCBM electrode interface is expected to strongly impact charge transfer processes in photovoltaic devices. Here we report molecularly-detailed studies of PCBM ordering at coinage metal surfaces. We have developed a vacuum-compatible liquid delivery source to generate thin films of C₆₀- and C₇₀-PCBM from organic solvents. Structure is tracked from the sub-monolayer to multilayer regime on (111)-oriented Ag and Au surfaces with molecular detail by UHV-STM. Glassy morphologies of as-grown films reflect solvent retention. Upon thermal annealing solvent molecules are released and films evolve into ordered packing arrangements that depend upon the PCBM density in the original films. The hcp monolayer phase of C₆₀- and C₇₀-PCBM are newly produced and characterized, indicating the accessibility of new growth phases by μ -aerosol deposition.

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COLL 405

Zwitterionic macromolecules and their non-specific interaction reducing properties

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Supramolecular nanoassemblies that reduce non-specific interactions with proteins are of great importance for various biological applications. Recently, zwitterionic molecules are shown to reduce non-specific interactions with proteins because of their charge neutrality and strong hydration layer formation around zwitterions via electrostatic interactions. Design of amphiphilic macromolecules with zwitterions as hydrophilic functionalities results in a novel class of molecules, which are under explored. To address this, we have developed a new class of amphiphilic dendrimers with triazole based zwitterionic moieties as the hydrophilic functionalities and decyl groups as the lipophilic functional groups, which upon self-assembly expose zwitterionic groups to outer hydrophilic layer while tucking in the lipophilic alkyl chains. We hypothesize that this strategic incorporation of zwitterionic moieties into amphiphilic dendrimers renders the formed supramolecular aggregates protein resistant. As hypothesized we observed that zwitterionic dendrimers form micelle type aggregates with container properties. We have also demonstrated that these dendrimer aggregates reduce non-specific interactions with proteins of varying pI using Fluorescence and DLS studies.

COLL 406

Reactions of linear and cyclic ethers on Si(100)-2x1

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The reactivity of a series of linear and cyclic ethers on the Si(100)-(2x1) surface was studied using Auger electron spectroscopy and temperature programmed desorption mass spectrometry. Some computational modeling using surface cluster models was also employed to probe potential reaction pathways. All the ethers studied appear to have a thermally accessible dissociative adsorption channel via cleavage of a C-O bond after an initial weak interaction between the oxygen and the surface silicon dimer. Bifunctional cyclic ethers containing the alkene functionality produce a mixture of products, resulting from either oxygen-end addition or [2+2]-like addition. Bifunctional cyclic ethers containing more than one ether functionality appeared to give rise to desorption products resulting from surface interactions through both ring oxygens. General reactivity trends and structure-activity relationships with respect to ether and alcohol chemistry and thermal decomposition on the silicon surface will be discussed.

COLL 407

Efficient charge transfer from excited state ruthenium dyes into colloidal nanoparticles as a model for dye sensitized solar cells

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The dye-sensitized solar cell is studied by focusing on the sensitizing dye adsorbed to colloidal nanoparticles. In this way, we study dye attachment, photoexcitation of the dye, and the subsequent electron injection, using NMR and transient absorption (TA) spectroscopy. Zinc Oxide (ZnO) dispersion-phase nanoparticles are used as electron acceptors and ruthenium-polypyridyl complexes as the dyes. Electron donating substituents on the ruthenium complexes were utilized to increase the excited state oxidation potential, promoting electron injection into the ZnO conduction band. TA spectroscopy on dye:nanoparticle dyads has shown an electron injection into 3 nm ZnO nanoparticles. Our study of the dye molecules' interactions with the nanoparticles provides details about the attachment, surface environment, and the ability for the dyes to inject electrons. We show that the lessons learned in our studies can be extrapolated to new dye designs that will reduce loss mechanisms with the aim of increasing efficiency.

COLL 408

Fabrication and characterization of gold nanoring and nanocrescent arrays as substrates for surface enhanced infrared absorption spectroscopy

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We designed substrates of two-dimensional arrays of gold nanorings and nanocrescents on large areas based on shaped nanosphere lithography for surface enhanced infrared absorption spectroscopy (SEIRA). In our nanosphere lithography approach two reactive ion etching (RIE) steps were used. In the first RIE process, oxygen gas reshaped polystyrene spheres. After metal deposition, the second argon plasma etch of exposed metal yielded arrays of nanorings. To form crescents, we used a non-conductive strip placed on the sample edge to bend argon ion flow during the second RIE. Arrays were characterized by scanning electron, atomic force and infrared microscopes. The dimensions of ring-like structures ranged from 170 to 350 nm. Samples were highly uniform, densely packed ($7 \times 10^8 \text{ cm}^{-2}$) and exhibited tunable plasmon resonances in mid-infrared region. These characteristics made the arrays ideal substrates for SEIRA. Therefore, we used them to study SEIRA of molecules such as octadecanethiol.

COLL 409

SERS based charge transfer probing of micron sized anatase TiO₂ through organic linkers with silver nano-particles

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We present a direct probe of the charge transfer interaction on a micron sized anatase TiO₂ crystal using a linker molecule and silver nanoparticles. All linker molecules were either a di-thiol or a thiol with a carboxylic acid. The dithiol system allows for the TiO₂/silver band gap to work as the driving force behind the charge transfer mechanism, while the thiol/carboxylic acid system establishes a dipole that can enhance or stop the charge transfer from TiO₂. Bulk Raman spectra indicate that the TiO₂ charge transfer does contribute to the SERS, but that the silver plasmon still contributes the majority of the Raman enhancement. SEM was used to confirm the structure and coverage.

COLL 410

Bioreducible insulin-loaded nanoparticles and their interaction with model lipid membranes

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To improve design processes in the field of nanomedicine, *in vitro* characterization of nanoparticles with systematically varied properties is of great importance. In this study, surface sensitive analytical techniques were used to evaluate the responsiveness of nano-sized drug-loaded polyelectrolyte complexes when adsorbed to model lipid membranes. Two bioreducible poly(amidoamine)s (PAAs) containing multiple disulfide linkages in the polymer backbone (SS-PAAs) were synthesized and used to form three types of nanocomplexes by self-assembly with human insulin, used as a negatively charged model protein at neutral pH. The resulting nanoparticles collapsed on top of negatively charged model membranes upon adsorption, without disrupting the membrane integrity. These structural rearrangements may occur at a cell surface which would prevent uptake of intact nanoparticles. By the addition of glutathione, the disulfide linkages in the polymer backbone of the SS-PAAs were reduced, resulting in fragmentation of the polymer and dissociation of the adsorbed nanoparticles from the membrane. A decrease in ambient pH also resulted in destabilization of the nanoparticles and desorption from the membrane. These mimics of intracellular environments suggest dissociation of the drug formulation, a process that releases the protein drug load, when the nanocomplexes reaches the interior of a cell.

COLL 411

Electrical properties of vertically- aligned ZnO nanowires investigated by current sensing AFM and Kelvin probe force microscopy

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We present a simple method for generating arrays of vertically-aligned ZnO nanowire (NW) arrays with tailored electrical properties, suitable for photodetector and photovoltaic applications. ZnO NWs were synthesized on Si substrate using a hydro-thermal method, producing dense and highly organized vertical ZnO NW (~100 nm) arrays as revealed by SEM. The vertical geometry of the NW arrays facilitated further processing of the NW structures and streamlined *in-situ* characterization of individual NWs as well as entire NW ensembles. The I-V characteristics of the ZnO NWs were measured using current-sensing atomic force microscopy, where an AFM tip made contact with individual metalized ZnO NWs while the growth substrate provided the back contact. Compared with arrays of as-grown ZnO NWs, the metalized top contacts of NWs resulted in improved I-V characteristics with good rectifying behavior, attributed to Schottky barrier formation for the gold deposition and stable ohmic contact formation for aluminum and gold.

COLL 412

Linear-dendritic copolymer micelles for multivalent targeting

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Multivalent interactions play a critical role in cellular biochemistry. We have developed a novel approach to control the arrangement of cell-targeting ligand on nanoparticle surfaces using linear-dendritic copolymeric (LDP) system that self-assembles into micelles, the surface of which bears specific number of ligands in a clustered pattern. Previously our group has reported the synthesis and biological assessment of such "Patchy" micelles for the first time, where the targeting ligand folic acid was clustered on the micellar surface [1]. It was found that both cellular uptake and tumor accumulation of these micelles critically depends on the number of targeting peptides per cluster.

In this project we have immobilized a cancer cell targeting peptide, Lyp-1 (CGNKRTRGC) [2] on a linear-dendritic copolymer through Cu-mediated azide-alkyne click chemistry. As a linear block, poly(β -benzyl aspartate) was utilized which was attached to a generation 4 polyester dendron. The stoichiometric mixing of Lyp-1 functionalized and unfunctionalized LDP molecule results in micelles with a definite number of Lyp-1 arranged over the micellar surface in a clustered pattern. The micelles were within the size range of 80-90 nm with a CMC in the order of 10^{-5} M. The Lyp-1 peptide bearing micelles showed higher uptake in MDA-MB-435 cell line compared to the unfunctionalized micelles, indicating ligand-mediated uptake. It was found that

though the average number of ligands per micelles is the same, cellular uptake in MDA-MB-435 cells was dependent on the number of Lyp-1 per cluster, indicating the spatial affect of molecular crowding on ligand-receptor engagement.

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COLL 413

Interactions of gold nanoparticles with mitochondria and Cyt c using Resonance Elastic Light Scattering and Fluorescence techniques

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Injuries caused by oxygen deficit and reperfusion are deleterious to the cells and are involved in serious illnesses including heart attack, stroke, Alzheimers, and others. During hypoxia, the mitochondrial matrix is swelling and cytochrome c (Cyt c) is released to the cytosol, marking the beginning of cell apoptosis. In this work, we have investigated electrostatic interactions of mitochondria with thiol-capped gold nanoparticles (AuNP) evidenced by the bathochromic shift of the local surface plasmon (SP) and changes in resonance elastic light scattering (RELS) intensity. The interactions of hemoprotein (Cyt c) and coenzyme Q with nanoparticles have also been investigated. The effect of various drugs influencing the potassium ion-channel opening and inner mitochondrial membrane polarization have been analyzed to elucidate the mechanisms of reduced sensitivity of some cells to hypoxia and reperfusion conditions. The RELS spectroscopy and fluorescence spectroscopy have been employed in measurements.

COLL 414

Synthesis and Characterization of Poly(caprolactone)-based X-ray Imaging Polymer Systems

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With two of the most common processes for imaging in the human body being general X-ray radiography and computed tomography (CT) technologies, researchers are exploring and developing new imaging agents and novel nanoscale vessels as alternatives to traditional unspecific small molecule, high dosage therapies and contrast agents. Our undergraduate-only research lab at College of Charleston is preparing

functional poly(epsilon-caprolactone) systems with engineered X-ray opacity (from grafted small molecules) and water-solubility (from grafted poly(ethylene oxide) chains) via oxime and thiol-ene “Click” chemistries. This presentation will focus on our synthetic efforts and our cumulative characterization of the novel materials by proton and carbon nuclear magnetic resonance (NMR), infrared (IR) spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis in addition to our characterization of the iodine-loading in the polymer samples to afford x-ray opacity.

COLL 415

Humidity dependence in silane monolayer patterning via atomic force microscopy

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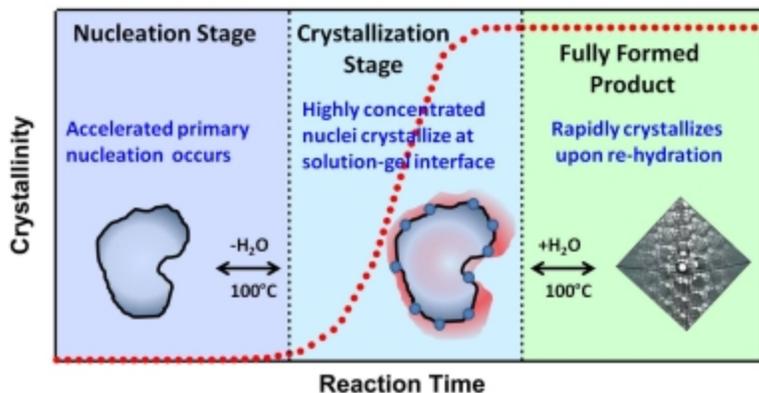
The ability to consistently create nanometer-sized patterns is essential for the development of molecular electronics and better biosensors. Due to their robust nature silane monolayers are widely used to create uniform surfaces. In order to effectively pattern these surfaces, all the parameters that impact the process must be optimized. Here in, two self-assembled monolayers (SAMs) were formed on a SiO₂/Silicon(100) substrate, octadecyltrichlorosilane (OTS) and octadecyldimethylchlorosilane (ODMS). These SAMs were characterized using goniometry, ellipsometry, and atomic force microscopy (AFM). Different binding structures in these SAMs lead to drastically different results when patterning with an AFM cantilever. In addition to clear dependencies on tip sharpness and applied force, patterns created in both monolayers demonstrate an increased ease of removal under greater ambient humidity, indicating that the dependence could stem from the catalytic role of water in silane SAM formation. These patterns and the precise role of ambient humidity are being investigated.

COLL 416

Rapid crystallization of zeolite-Y (FAU)

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A method is described in which highly crystalline zeolite Y (FAU) is rapidly synthesized. A custom reactor is designed to cycle the H₂O/Na₂O *in situ* during the synthesis between 57.4 and 33.2. We demonstrate that this method yields crystalline zeolite Y in one quarter the time of traditional hydrothermal routes: 110min versus 450min respectively. The kinetics are further accelerated through dropwise addition of amines. We conclude our method allows the simultaneous optimization of both the nucleation and crystallization growth stages.



COLL 417

Ligand design and construction of a tunable AuNP-based MRI contrast agent

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Movement towards nanostructures as the primary platform for MRI contrasts has been evident in recent years. The ability to load multiple lanthanide agents onto a single particle, thus increasing magnetic contrast and potentially lowering toxicity, makes nanoparticle platforms appealing in imaging applications. Here we demonstrate efficient construction of AuNP-based contrast agents using various high-yield ligands. Synthesis of novel “click”-ready passivating ligands, one-pot AuNP synthesis with these ligands, and conjugation of chelated lanthanide complexes are shown. Moreover, the use of these “click”-ready ligands allows for versatile conjugation of multiple moieties (chelated lanthanides, DNA aptamers, cell penetrating peptides, etc.). Stoichiometric control over the surface conjugation of these moieties is essential for biointegration of nanoparticle-based MRI contrast agents and is demonstrated here.

COLL 418

Supramolecular Assembly and Regulation of AIE Silole Molecules

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We study the noncovalent interaction tuned self-assemblies of Silole molecules bearing amino attachments (SI). The introduction of chiral amino acid attachments into silole backbone creates multiple chiral centers, which exert asymmetric force fields to the

silole, leading to the formation of helical filaments. By using AFM, we found that the helical fibers were best showed at relatively low concentrations (figure 1).

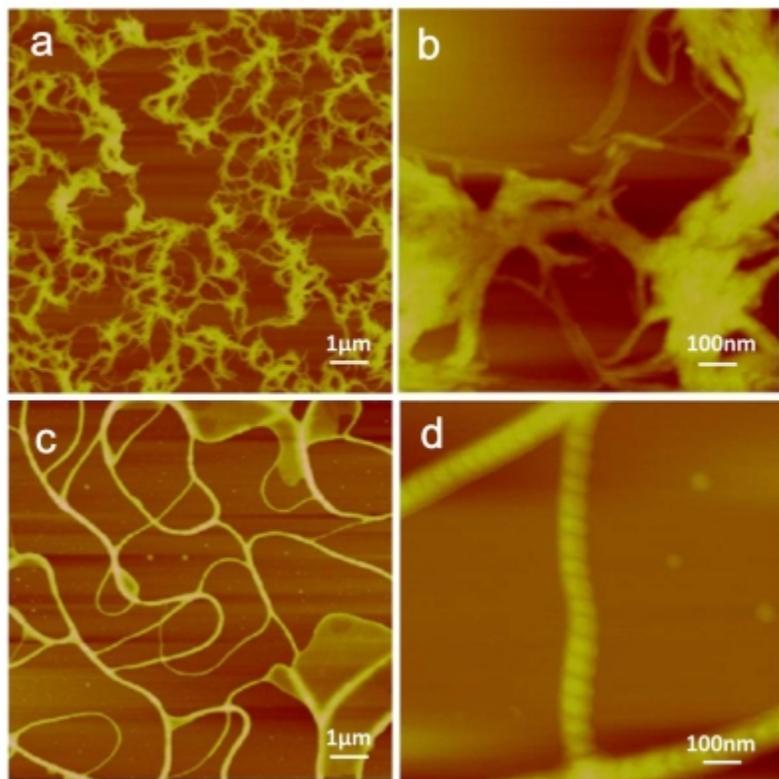


Figure 1 . AFM image of fibers formed upon natural evaporation of toluene solutions of SI on the surfaces of newly cleaved mica. Concentration of SI solutions:(a),(b) $150\mu\text{M}$, (c)~(d) $0.0015\mu\text{M}$

The assemblies can also be tuned by changing the ratios of the mixed solvents (figure 2).

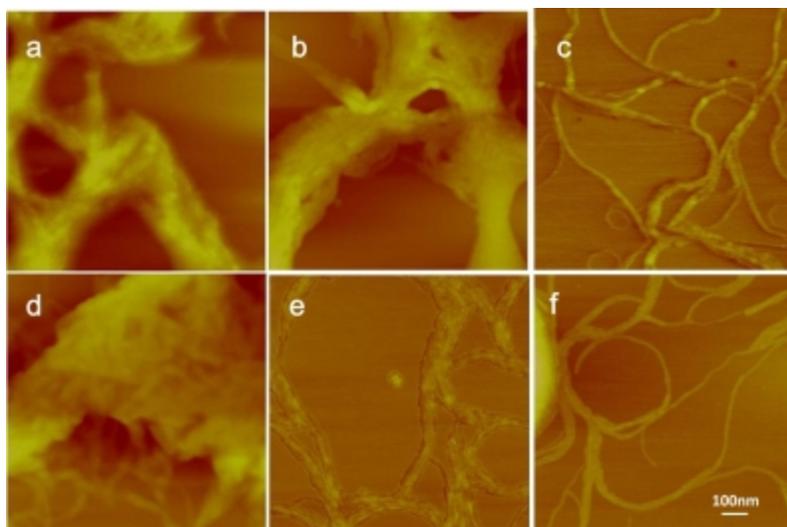


Figure 2 . AFM image of fibres formed upon natural evaporation of (a), (d) toluene (b), (e) toluene/acetonitrile (1:1,1:2 by volume), (c) toluene/THF (1:1 by volume), (f) toluene/acetonitrile/THF(1:1:1 by volume) solutions of SI on the surfaces of newly cleaved mica. Concentration of SI solutions:(a)~(c) 75 μ M, (d)~(f) 50 μ M

COLL 419

Effect of reducing agent on synthesis of palladium nanoparticles assemblies

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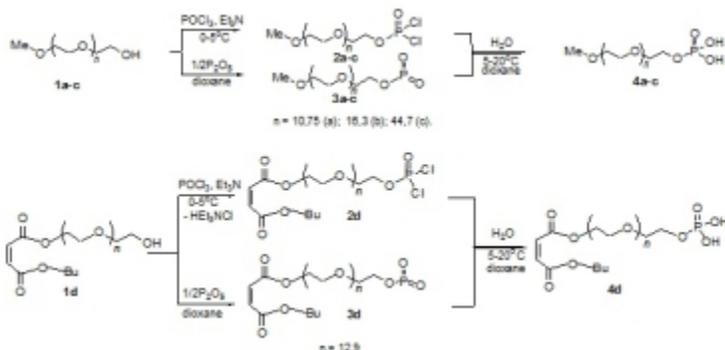
After previous successful synthesis of *in-situ* generated gold nanoparticles on silicon surfaces using an aminosilane monolayer, focus shifted to potential application of the procedure toward palladium nanoparticles synthesis. Initial trials with sodium citrate as reducing agent resulted in palladium nanoparticles with no catalytic activity. As a result, new reducing agents like formic acid and sodium borohydride are explored. The resulting surface bound palladium nanoparticles are characterized by Atomic Force Microscopy (AFM), UV-visible spectroscopy and surface zeta potential measurements. Additionally, palladium nanoparticle assemblies generated by different reducing agents are used to investigate relative catalytic efficiency for oxidation of higher molecular weight alcohols and polyalcohols that has direct significance for direct alcohol fuel cells (DAFCs).

COLL 420

Synthesis of surface-active phosphates

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The interaction of polyethylene glycole monomethyl eters of different molecular weights (550, 750 and 2000 g/mol) with phosphoryl chloride or with phosphorus (V) oxide has led to formation of corresponding monomethyl eters polyethylene glycole (MME PEG) phosphates. Maleic monomer with terminated phosphate group has been synthesized.



Characteristics of monomethyl eters with phosphate groups					
Compound	Yield, %	Expected/Found			Molecular formula
		Acidic number	C, %	H, %	
4a	94,4	178,1/169,5	46,76/45,51	8,27/8,02	C _{24,6} H _{52,1} O _{15,8} P
4a*	96.0	178,1/167,1	46,76/45,18	8,27/8,42	C _{24,6} H _{52,1} O _{15,8} P
4b	90.0	135,18/129,2	48,63/47,87	8,47/8,77	C _{33,6} H _{70,3} O _{20,3} P
4c	83.8	53,94/48,6	52,18/51,95	8,84/8,13	C _{90,5} H _{183,9} O _{48,73} P

* product received by the method b

The obtained compounds exhibit surface active properties and may be used for colloid nanomaterials stabilization.

COLL 421

One-step synthesis of thermally responsive mixed polymer brushes

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A new and efficient technique for the synthesis of mixed thermally responsive polymer brushes is reported. This technique is unique in that responsive layers of varying thickness (30nm-100nm) can be chemically anchored in a 1-step fashion to various substrates using grafting of block copolymers. To this end, a series of two block copolymers were synthesized bearing poly(glycidyl methacrylate) (PGMA) blocks of varying molecular weight, and a constant length poly(N-isopropylacrylamide) and poly(ethylene glycol) (PEG) segments. The PGMA component serves as the anchoring block via covalent attachment due to PGMA epoxy functionalities and complimentary substrate surface chemical groups. This technique allows for 1-step modification of a wide variety of organic and inorganic surfaces, as long as the surface contains functionalities reactive with epoxy groups. Surface properties and characterization of the resulting 1-step mixed brush synthesis is compared with mixed brush fabrication in 2- and 3-step processes. Atomic force microscopy (AFM), ellipsometry, dynamic contact angle, protein adsorption and adhesion were used to characterize the resulting polymer films.

COLL 422

Investigating phosphonate monolayer stability in aqueous solution

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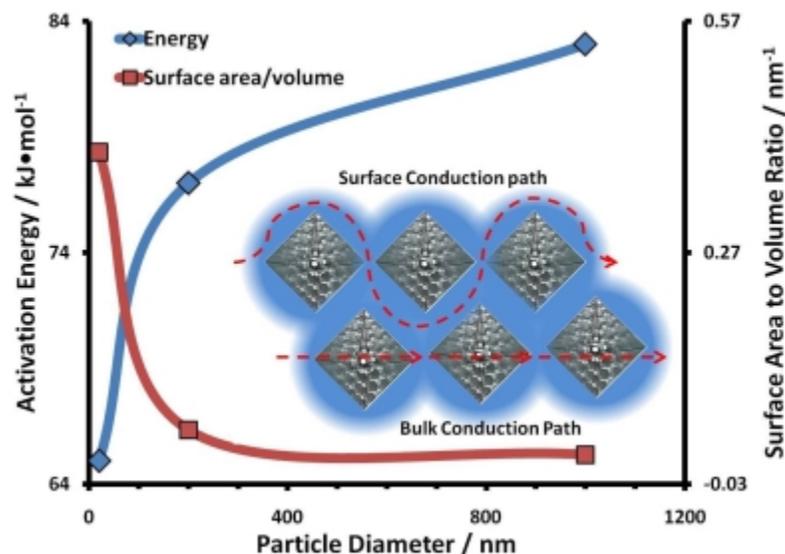
Organophosphonic acids have recently been explored as protective coatings in biosensors. In this study we investigate deposition of octadecylphosphonic acid and perfluorophosphonic acid on various oxide layers and characterized them by water contact angle, ellipsometry, x-ray photoelectron spectroscopy, and atomic force microscopy. The stability of these monolayers was investigated in water and phosphate buffer. We found that the monolayers on SiO₂ and TiO₂ exhibited significant surface reorganization upon exposure to water. SAMs formed on Al₂O₃ and HfO₂ were much more stable where Al₂O₃ showed short-term stability (up to 10 days) in water, while SAMs on HfO₂-coated surfaces were stable for more than 10 days under aqueous conditions. Furthermore, PFFPA SAMs on HfO₂ were found to be the most stable SAMs studied here with up to 20 days of stability in water. These results demonstrate the longest stability in aqueous conditions for any reported phosphonate SAM on an oxide surface.

COLL 423

Size dependent ionic conductivity of zeolite

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The ionic conductivity of aluminosilicate zeolite Y was studied as a function of particle size. Impedance spectroscopy data obtained from particles of ~ 600 nm, 200nm, and 40nm indicate higher conductivities for smaller particles with activation energies of 83, 75, and 66 kJ/mole, respectively. A model using parallel surface and bulk conductivity was developed to explain these observations.



COLL 424

Direct visualization of the Disassembly of polyphenylacetylene carrying Valine Attachments Tuned by a pH Change

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We utilized fluorescence microscope in the detection of pH-switching effect of L-valine containing polyphenylacetylene (PPA-Val) by binding the helical polymer chains with Ru (II) complexes. We revealed an in situ and realtime unraveling process of the helical assemblies of PPA-Val stimulated by addition of KOH to its solution with fluorescence microscope.

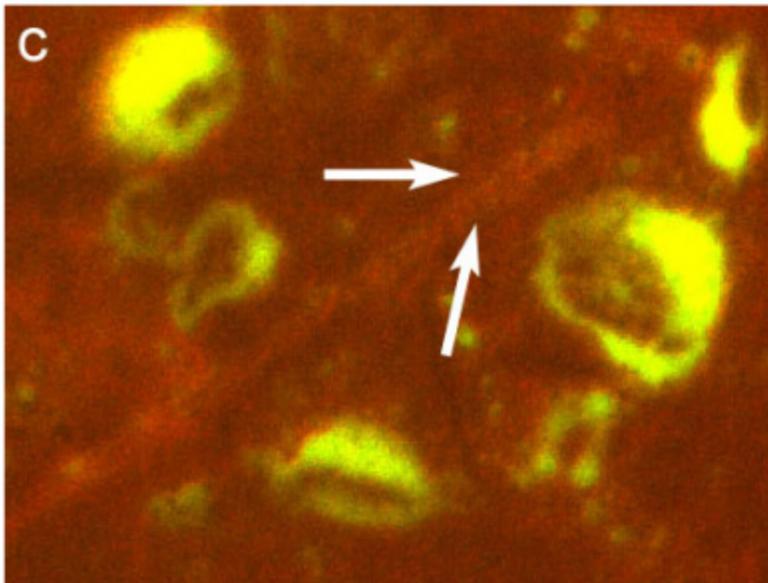
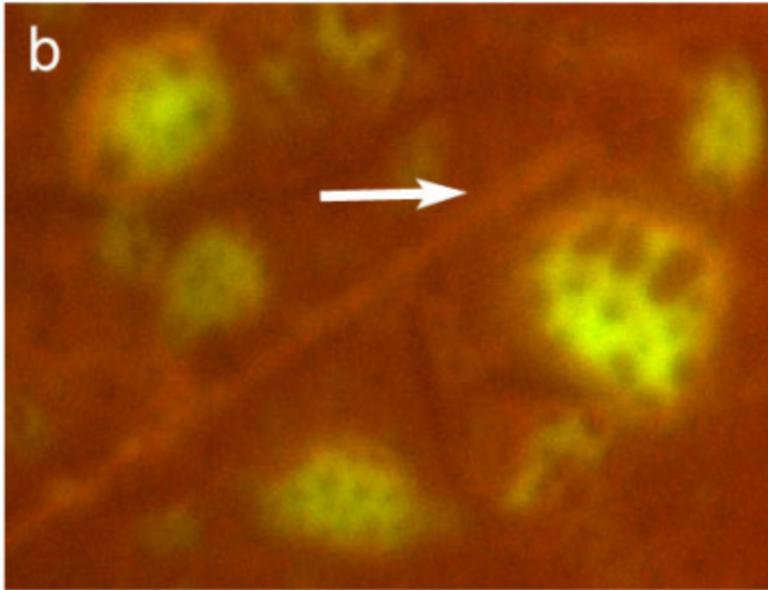
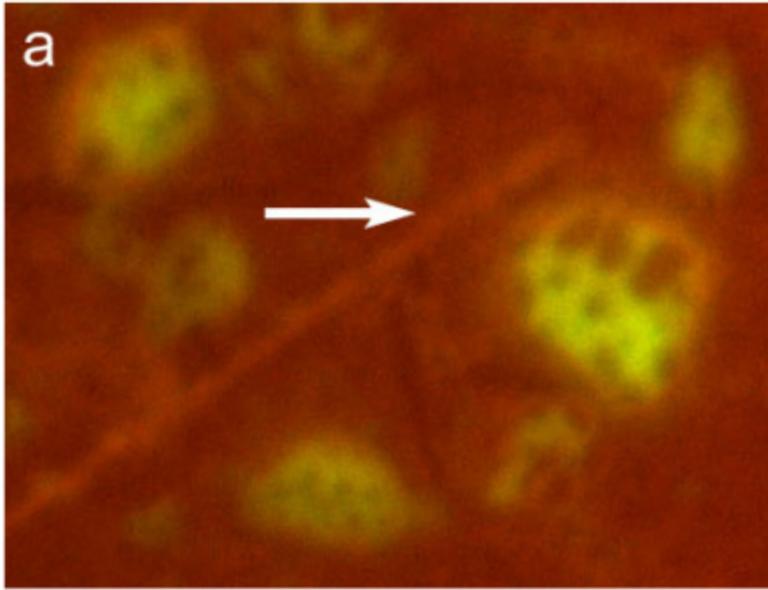


Figure 1. In situ and realtime fluorescence images of the unraveling of the assemblies formed by PPA-Val into loose loops with addition of KOH to its water solution. image **a** was recorded at 0 time without adding KOH, the images **b** and **c** were recorded with addition of KOH after 10 seconds, 20 second.

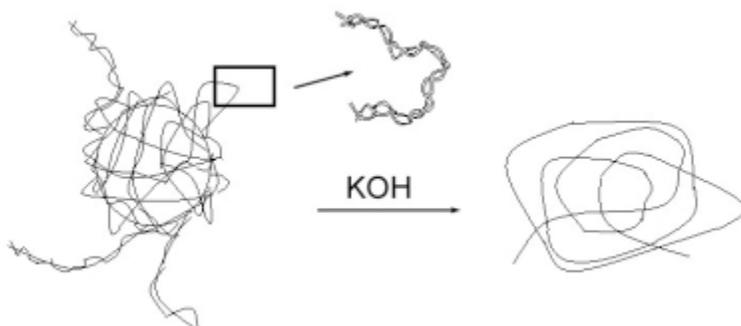


Figure 2 Disassembly of the superhelices of PPA-Val induced by a variation of pH. The entanglements of the helical assemblies were unraveled into loose loops.

COLL 425

Ionic Strength and Specific Ion Effects on Antimicrobial Peptide Activity

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The effect of ionic strength on the activity of a family of designed antimicrobial peptides was measured for a panel of microorganisms. The minimum sterilizing concentrations (MSC) were found to vary linearly with ionic strength for a variety of ionic species. [figure 1] In addition, specific ion effects were observed for MgSO₄ which was later shown to be due to the divalent Mg²⁺ ion. The MSC values for our peptides against four microorganisms were determined in the presence of divalent Mg and Ca ions. Specific ion effects were observed to occur in different concentration ranges in an organism dependent fashion.

COLL 426

Investigation on the Removal of Zn Ion by Solvent Sublation

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Solvent sublation, originally introduced by Sebba, has shown promising features for removing hydrophobic compounds and ions from aqueous systems. The removal of the Zn ion as the Zn-dithizone complex, $[(C_{13}H_{12}N_4S)_2Zn^{2+}]$, from aqueous solutions was studied based on the solvent sublation of $[(C_{13}H_{12}N_4S)_2Zn^{2+}]$ -cetyltrimethyl ammonium bromide (CTAB) (sublate) into isopentanol. The experimental conditions, such as the pH, the ratio of surfactant to Zn complex and the effects of electrolytes, were optimized. More than 98% Zn ions can be removed from the aqueous solution within 1 hr with the ratio of 5:1 of surfactant to Zn-dithizone complex. The removal efficiency increased dramatically with the treatment of 0.5 M NaCl. The removal rate was somehow enhanced at higher airflow rate. Further, it was independent of the volume of the organic solvent floating on the top of the aqueous column. According to thermodynamic studies, this process is consistent with the first order kinetics. The apparent activation energy of the attachment of sublates to bubbles was estimated to be 9.04 kJ/mol. A mathematical model for the $[(C_{13}H_{12}N_4S)_2Zn^{2+}]$ -surfactant was obtained based on the complete transport mechanism. In addition, the simulation of the mathematical and experimental data was consistent.

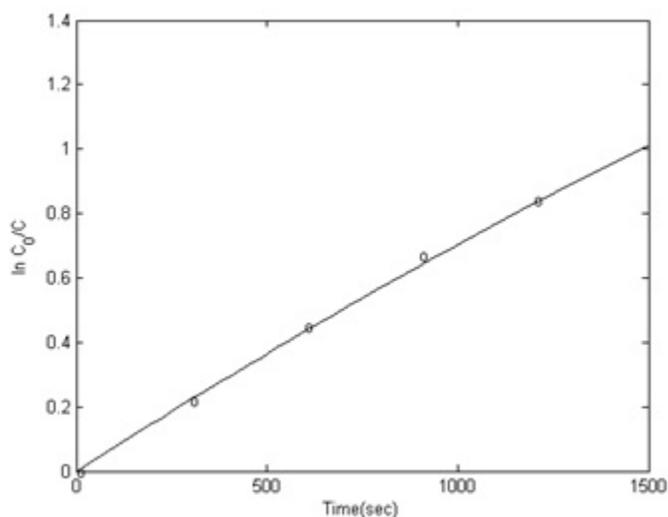


Figure 1. Simulation of experimental results for the solvent sublation of $[(C_{13}H_{12}N_4S)_2Zn^{2+}]$ -CTAB, the line represents for the theoretical result; the circle represents the experimental result, $C_{Zn} = 2.55 \times 10^{-5}$ mol/L; $C_{CTAB} = 1.275 \times 10^{-4}$ mol/L.

Surgery-like-induced fusion of droplets in microchannels for preparing microspheres and microcapsules

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The on-demand fusion of diverse microdroplets in microfluidic systems can be employed as microreactors to perform a range of chemical and biological reactions. However, current techniques of droplet fusion are mostly triggered by special channel design, electrical fields or lasers. These methods are either complicated to construct or difficult to control. Here we report a novel and simple surgery-like-induced approach to control the fusion of surfactant-stabilized droplets in microchannels. When two droplets flow across a lancet-like mechanical component embedded in convergence microchannel simultaneously, they will be adsorbed and scratched on the surface, which causes the change in surface tension to induce fusion of the two droplets. In this method, the fusion of water-in-oil emulsions and multi-core oil-in-water-in-oil emulsions are successfully demonstrated for the first time, from which the chitosan microspheres and microcapsules are prepared. Our technique also could be potentially applied in microreactors, high-throughput reagent injection, etc.

COLL 428

Thiol/disulfide rationale to formulate therapeutic biopolymer nanomaterials

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Thiolation of biopolymers is known to improve mucoadhesion, targeted tissue permeation and enzyme inhibition. Ambiguously, highly thiolated biopolymers display in situ gelling properties due to oxidative inter- and intra-molecular disulfide cross-linking. In order to exploit the reversible thiol-disulfide interconversion at a nanometer scale various thiolated biopolymers were processed into nanomaterials of different design. Nanoscale surface coatings were deposited on gold in a layer-by-layer fashion using cationic thiolated chitosan and glycosaminoglycan counterions. In another approach, nanoparticles were developed from thiolated biopolymers in a one-step sonochemical process. In both cases the degree of biopolymer thiolation was identified as a key factor controlling the thickness of the coating and the size of the nanoparticles. Additionally, the exploitation and therapeutic properties, e.g. biostability, drug delivery, cell-material interactions, and enzymes inhibition, of these novel nanomaterials were tunable by the thiol/disulfide ratio.

COLL 429

Formulation of hybrid biopolymer hydrogels containing phenolic nanoparticles

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Processing of bioactive molecules into nanoscaled particles (NPs) ensures their improved bioavailability and reduced dose administrations. Additionally, in order to control the localized drug delivery, these nanotherapeutics are used in combination with implantable medical devices. An ideal NPs therapy should provide effective and continuous therapeutic doses over extended periods of time. In this study, nanotherapeutics from various polyphenolic compounds were formulated under sonication. Moreover, hybrid hydrogel-nanotherapeutics devices were obtained by dispersion of polyphenolic NPs in biopolymer solutions prior to their *in situ* auto- or enzymatically induced gelation. The *in vitro* NPs release profiles from the platforms were found to be tunable by the gelation mechanism used, e.g. disulfide or enzymatic cross-linking. Finally, the hybrid systems were evaluated for their biocompatibility, capacity to inhibit deleterious wound enzymes and potential to induce wound closure in a specially designed ex-vivo wound model.

COLL 430

Combined antimicrobial/antifouling coatings using zwitterion-decorated phenolic nano-capsules

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More than 60% of bacterial infections currently treated in hospitals are related to the formation of biofilms, which are bacterial communities encased in a self-produced hydrated polymeric matrix. In this study, nanoscale capsules (NCs) made of plant polyphenols have been sonochemically generated and/or loaded with antimicrobials. Thereafter, these nanocarriers were enzymatically grafted on pre-aminated medical grade silicone. In a second step, the polyphenolic NCs were co-polymerized with zwitterionic vinyl moieties using laccase enzyme. As a result, a multifunctional surface was obtained combining: i) antibacterial activity of polyphenols, ii) anti-biofilm formation properties resulting from zwitterionic moieties and iii) potential drug delivery from the phenolic capsules. The successful generation of NCs and subsequent grafting on silicone and functionalization were evaluated by means of chemical, physical and spectroscopic techniques, while the efficiency of the resulting surfaces against biofilm formation was assessed *in vitro* against Gram- and Gram+ bacteria.

COLL 431

Wound dressing hydrogels with in-built antioxidant and antimicrobial systems

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Chronic wounds constitute a major health care problem all over the world partly attributed to persistent production of free radicals and pathogenic bacteria. This work presents for the first time, a dynamic system which is able to continuously quench free radical and inhibit pathogens. This system is based on the ability of phenolic antioxidants to quench free radicals and the ability of cellobiose dehydrogenase (CDH) to reduce oxidized phenolic antioxidants back to the parent compound as well as the ability of CDH to use oxygen for production of hydrogen peroxide. *In vitro* incubation of radical generating system with phenolic antioxidants resulted in the oxidation of the respective phenolic antioxidants and addition of the antioxidant regenerating system resulted in the regeneration of the parent compound. Hydrogels loaded CDH hydrogels and supplemented with cellobiose completely inhibited the growth of *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas putida* and *Cellulomonas microbium cellulans*.

COLL 432

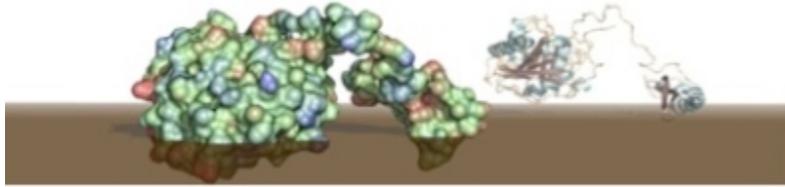
Re-design of cutinases to increase activity on Polyesters

Enrique Herrero Acero¹, *enrique.herreroacero@acib.at*, Doris Ribitsch¹, Annemarie Marold¹, Katrin Greimel¹, Georg Steinkellner¹, Karl Gruber¹, Helmut Schwab^{1,2}, Artur Cavaco-Paulo³, Georg M. Guebitz^{1,4}. (1) Austrian Centre of Industrial Biotechnology, Graz, Austria (2) Institute of Molecular Biotechnology, Graz University of Technology, Graz, Austria (3) Department of Textile Engineering, University of Minho, Graz, Austria (4) Institute of Environmental Biotechnology, University of Natural Resources and Life Sciences, Vienna, Austria

Among the enzymes described to hydrolyze synthetic polyesters, cutinases have been shown to be most active on PET. Recently we have identified two cutinases from *Thermobifida cellulolytica* (Thc_Cut1 & Thc_Cut2) having only few amino acid differences located outside the active site but yet showing very different kinetic parameters regarding hydrolysis of PET. Therefore, based on exchanges of these critical aminoacids we investigated their influence in hydrolysis of soluble and insoluble substrates and developed mutants more active towards PET.

We also fused two binding domains from a PHA-depolymerase from *Alcaligenes faecalis* (Thc_Cut1+PBM) and from cellobiohydrolase I from *Trichoderma reesei* (Thc_Cut1+CBM) to Thc_Cut1 in order to improve the sorption process on the polymer surface. We successfully cloned, expressed and characterized these enzymes in terms

of hydrolysis of soluble substrates and PET. It was possible to correlate an increase in adsorption measured with Quartz Crystal Microbalance with Dissipation (QCM-D) with a higher activity measured as soluble released products (HPLC-UV).

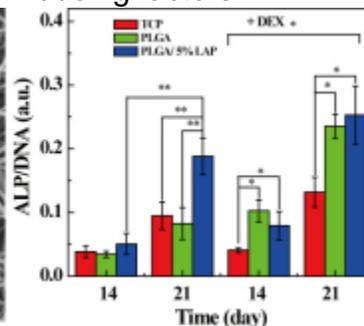
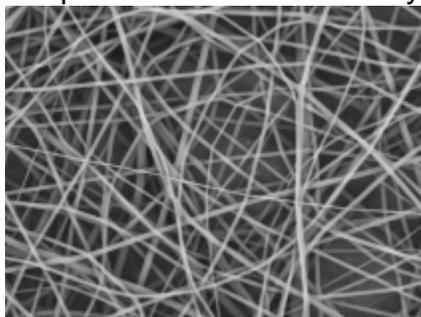


COLL 433

Osteogenic differentiation of human mesenchymal stem cells onto electrospun laponite-doped poly(lactic-co-glycolic acid) nanofibers

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We report the fabrication of laponite (LAP)-doped poly(lactic-co-glycolic acid) (PLGA) nanofibers for osteogenic differentiation of human mesenchymal stem cells (hMSCs). In this study, LAP-doped PLGA nanofibers were formed via simply electrospinning the mixture solution of PLGA and LAP. We show that the incorporation of LAP does not significantly change the uniform PLGA fiber morphology, instead significantly improves the mechanical durability of the nanofibers. The surface hydrophilicity and protein adsorption capacity of the composite nanofibers slightly increase after doping with LAP. Cytocompatibility results reveal that the incorporated LAP is beneficial to promote the cell adhesion and proliferation likely due to the improved surface hydrophilicity and protein adsorption capability of the fibers. Finally, we demonstrate that the doped LAP within the PLGA nanofibers is able to induce the osteoblast differentiation of hMSCs in complete medium without any inducing factors



. The fabricated LAP-doped PLGA nanofibers may find many various tissue engineering applications.

COLL 434

Sugar-selective imaging of mannose by atomic force microscopy using probe tips modified chemically with concanavalin A

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We have successfully accomplished a sugar-recognition imaging at high-resolution by atomic force microscopy (AFM) using probe tips functionalized chemically with concanavalin A (ConA). The specific unbinding force between mannose and ConA can be observed by AFM force measurements using the ConA-modified probe tip. We can utilize the ConA-modified AFM tip to obtain sugar-selective images on a substrate with artificial pattern of sugars based on the specific interaction force between ConA and the mannose moiety on the substrate. We demonstrate that the image contrasts can be attributed to the sugar recognition by the ConA immobilized onto the AFM probe tip. In addition, a similar sugar-recognition imaging was conducted on quasi biological membranes with a phosphorylcholine group using the ConA-modified AFM tip.

COLL 435

Determining Avidity Distribution of Ligand-functionalized Multivalent Nanoparticles Using SPR Kinetic Analysis

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Multivalent interactions have been used for a number of biomedical applications involving targeted therapy and imaging. We attempted to develop design guidelines for multivalent interactions by examining the effects of valence and the affinity of ligands on multivalent interactions of synthetic nanoparticles where the affinity is modulated using programmable ssDNA sequences as ligands. We then measured kinetic parameters of nanoparticles with complementary oligonucleotides using SPR. These interactions resulted in reproducible kinetic curves with biphasic behaviors, including both a fast dissociation and a slow disassociation that was irreversible during the time course of experiments. We also developed kinetic analyses to quantify the molar fraction of nanoparticles demonstrating different behaviors and identify their avidities. These

analyses demonstrated that valence number of the nanoparticle and the ligand affinity both markedly affect multivalent interactions. Our results suggest multivalent nanoparticles functionalized with μM -affinity high-valence ligands show enhanced multivalent interactions and targeting efficacy.

COLL 436

Preparation and characterization synthetic polymer ligands that recognize target peptides with multipoint interaction

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It has been reported that synthetic polymer nanoparticles with optimized combination of functional monomer, such as hydrophobic or charged monomer, can bind and neutralize toxic peptides. Some of the particles are capable of recognizing and neutralizing the target peptide even in the bloodstream of living animals. However, neutralization capacity in vivo was significantly lower than that in vitro. One of the considerable reasons is the nonspecific binding of serum proteins competing with binding of the target peptides. To utilize the materials in the biological milieu, design of synthetic materials with higher specificity are required. Here, we suggest linear polymer ligands that recognize target peptide with multipoint interaction. Reversible addition-fragmentation chain-transfer (RAFT) polymerization was employed to synthesize multifunctional polymer ligands with much lower molecular weight and polydispersity index (PDI) than nanoparticles, enabling much narrower diversity of polymer structure. Prepared linear polymer ligands showed different affinity and specificity to the target peptide, depending on the molecular weight and monomer compositions.

COLL 437

Surface modification on thiol-functionalized PDMS for potentially antibacterial biomaterials

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The surface hydrophobicity of polydimethylsiloxane (PDMS) can limit its use in biomaterials due to the significant adsorption of biological components. Several strategies to improve the hydrophilicity of PDMS are often compromised by hydrophobic recovery. We report controlled surface modification by the introduction of thiol groups onto PDMS surfaces and then modification of the surface by thiol-ene click reactions, and oxidation. The PDMS surface was first functionalized with thiol groups by base-catalyzed equilibrium treatment with $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OR})_3$. After maleic anhydride was introduced using thiol-ene click processes, a variety of surfactants and polymers were grafted via ester/amide formation. Residual thiols could be protected through oxidation,

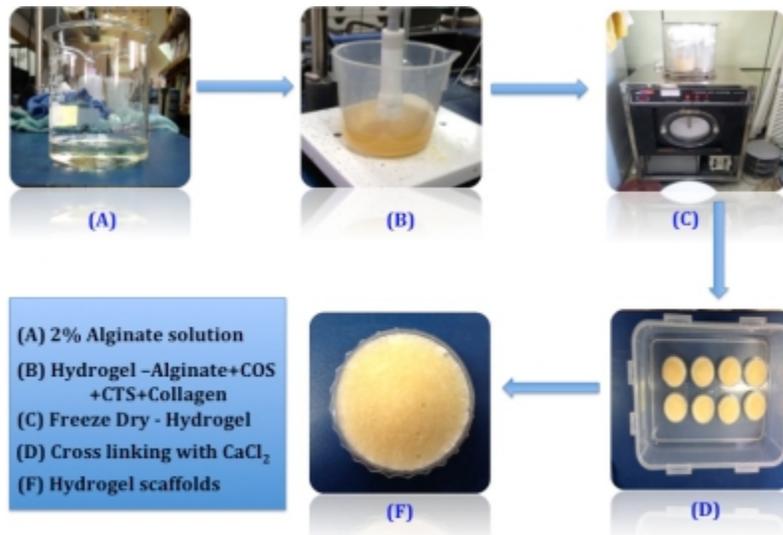
or undergo secondary reaction. The hydrophilicity of PDMS surface was improved. The ability of *E. coli* to adhere and propagate is affected by the nature of the surface, both with respect to hydrophilicity and the presence of different functional groups. These relationships will be discussed.

COLL 438

Chitosan based hydrogels for bone tissue engineering

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In the recent era, significant development has been achieved in the research field based chitosan hydrogels for bone tissue engineering. In the present study, we have prepared and analyzed different kind of hydrogels by the combination of carbon nanotube and collagen with chitosan, and also *in vitro* biomineralisation was (hydroxyapatite coating) attained on the hydrogels by stimulated body fluid. The prepared hydrogels are chemically characterized, and *in vitro* studies are performed with osteoblastic (MC3T3-E1) cell line and *in vivo* study. The obtained results infer that the prepared hydrogels are non-toxic and higher proliferation was observed on the ternary hydrogels. As the conclusion, by the addition of collagen, carbon nanotube and hydroxyapatite in the chitosan hydrogel, improved properties was observed to mimic the nature function of bone.



COLL 439

Chlamydia major outer membrane protein (MOMP) induces high IFN- γ and T-cell proliferative responses in mice

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Chlamydia trachomatis genital infection is a worldwide public health problem. Overall, 4 million *Chlamydia* cases were reported to the CDC in 2010. Considerable effort has been expended on developing an efficacious vaccine. The murine model of *C. trachomatis* genital infection has been extremely useful for identification of protective immune responses and in vaccine development. Although a number of immunogenic antigens have been assessed for their ability to induce protection, the majority of studies have utilized the whole organism and its major outer membrane protein (MOMP) as vaccine candidates. MOMP is the most immune-stimulatory protein identified to date, but it does not induce sterile protection and at the same time it is reported to be immunosuppressive in nature. To begin to identify the immune-stimulatory regions with T-cell epitopes, we immunized three groups of mice at two-week interval as follows: (i) Group 1 (PBS + incomplete Freund's adjuvant) (ii) Group 2 (live *C. trachomatis*) (iii) Group 3 (rMOMP + incomplete Freund's adjuvant). Mice were sacrificed two weeks after the last immunization, and purified T-cells isolated from spleens of immunized mice were restimulated *in vitro* with Concanavalin A, UV-inactivated *C. trachomatis* and rMOMP. T-cell samples from mice were analyzed by cytokine ELISA for IFN- γ production and the MTT assay for T-cell proliferation. Our results revealed that rMOMP-stimulated T-cells induced maximum production of IFN- γ and proliferation as compared to the PBS and *C. trachomatis* immunized groups. Studies are ongoing to identify the specific immune-stimulatory regions of MOMP.

COLL 440

Enhancement of activity of antioxidants by platinum nanoparticles catalysis

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Some of nanoparticles exhibit antioxidant activities and are expected their new beneficial application, although many researches are focusing on toxicity and safety of metal nanoparticles. We previously reported superoxide anion radical- and hydroxyl radical-scavenging activities of platinum nanoparticles (Pt NPs) *in vitro*, demonstrating intracellular reactive oxygen species (ROS)-scavenging activity of Pt NPs using cultured

animal cells. Here we show another aspect of Pt NPs as antioxidants. There is a possibility that Pt NPs enhances only atomic hydrogen transfer reactions in cells because of reductive atmosphere are maintained by the intracellular redox regulation system. Actually, Pt NPs enhanced DPPH radical and ROS scavenging reaction of reduced glutathione and ascorbic acid in vitro. In this presentation, we will show the influence of Pt NPs on reaction by biological antioxidants in stoichiometric and kinetic study, discussing the correlation of intracellular ROS-scavenging activity and Pt NPs-enhanced antioxidant activity.

COLL 441

Analysis of mechanism of intracellular reactive oxygen species-scavenging activity by platinum nanoparticles

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Most of studies using nanometer-sized metal particles have focused on biological safety and potential hazards. However, we previously reported that platinum nanoparticles (Pt NPs) could scavenge reactive oxygen species (ROS) such as superoxide anion radical and hydroxyl radical, demonstrating intracellular ROS-scavenging activity of Pt NPs using cultured animal cells. In this study, we analyzed intracellular ROS-scavenging activity of Pt NPs in more details. Pt NPs did not show cytotoxicity on rat myoblast cells below 10 ppm. Pt NPs scavenged intracellular H₂O₂ dose-dependently. In addition, Pt NPs increased the amount of intracellular glutathione in the range of 0.01-1 ppm. Pt NPs also upregulated antioxidant-related gene expressions, suggesting that Pt NPs uptaken into cells regulate redox signaling pathways because Pt NPs scavenged intracellular ROS significantly even in a concentration as low as 0.01 ppm. The mechanism of action of Pt NPs will be discussed

COLL 442

Dielectrophoretic Manipulation and Assembly of Colloidal Particles

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Manipulating the particle concentration is of great importance for the overall behavior for colloidal systems as well as the other soft matter systems such as polymers, biomaterials, emulsions, and liquid crystals. Gravity and temperature gradients have been used to control the particle concentration in colloidal systems which are difficult to be precise. Here, we demonstrate the electric bottle composed of uncharged colloidal

particles which can be manipulated by dielectrophoretic forces in a confined space. It provides much better ability to precisely manipulate and assemble particles by tuning the nature of the electric fields such as frequency, field gradients, charge of the particles, and dielectric constant. By creating an array of cascaded electrode we can make a broader electric field gradient and speed up the assembling process. Furthermore, electric bottles with on-chip electrodes and microfluidics can be used for bioassays by manipulating cells or biomolecules.

COLL 443

Vertically aligned Hematite ($\alpha\text{-Fe}_2\text{O}_3$) nanotubes by electrochemical anodization for water splitting applications

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Functional nanostructured metal oxide semiconductors (n-MOS) of band gap fall in the visible spectrum are actively sought as photocatalyst to enable efficient splitting of water for hydrogen production. Among the many n-MOS, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is arguably the most suitable one for water splitting reaction due to its band gap energy (~2.2 eV) that falls in the high-intense side of solar spectrum, suitable band edges, high stability, possibility of producing mesoporous materials, and lower cost. However, due to high charge recombination and short hole transport distance the efficiency of the reaction is considerably reduced in nanostructured hematite particles. To overcome this drawback, alternate morphologies such as vertically aligned nanowires, which support channelled charge transport thereby reducing the recombination rate, are employed. In this research, hematite nanotubes were produced by anodizing iron sputter deposited on FTO coated glass substrates and characterized for their suitability for water splitting to enable solar hydrogen production.

COLL 444

Combining ligand design and photo-ligation to transfer hydrophobic quantum dots to hydrophilic media

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We describe the synthesis of a series of compact ligands made of multi-coordinating (lipoic acid based) anchors, polyethylene glycol or zwitterion groups, and tunable terminal functions. We combine these ligands with a novel photo-ligation strategy to promote the transfer of QDs to polar and buffer media using such ligands, where in-situ

reduction of the dithiolane, achieved under UV irradiation, is coupled with rapid ligand exchange on hydrophobic QDs. This strategy drastically improves previous transfer methods and is well adapted to the in-situ modification of QD surfaces with diverse functionalities. QDs with long term colloidal stability at sub-nanomolar concentrations under a range of biologically relevant conditions have been prepared and tested. This bodes well for in vivo imaging where very small concentrations are used. We also found that QDs stabilized with zwitterionic ligands are fully compatible with metal-histidine driven self-assembly with control the QD-protein conjugate valence.

COLL 445

Design of multidentate oligomeric ligands to enhance the biocompatibility of metal oxide nanoparticles

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We have developed a new versatile surface-functionalization strategy based on ligand exchange that is applicable to metal oxide nanoparticles (e.g., Fe₃O₄ NPs). This strategy involves the design of new set of multidentate dopamine oligomers prepared using one-step reaction of a short polymer backbone with lateral poly(ethylene glycol) short chains (or other hydrophilic moieties), and dopamine anchors. Here the catechol groups allow strong affinity to the iron oxide NPs, while dispersion in buffer media and biocompatibility is promoted by the PEG moieties. Ligand exchange of Fe₃O₄ NPs with these oligomers is remarkably efficient compared to other mono-coordinating capping molecules. The resulting NPs preserve their homogenous size and distribution and exhibit high colloidal stability over a broad range of conditions. Furthermore, our strategy allows the easy insertion of a controllable number of functional groups (e.g., amine or azide) on the NPs, making them compatible with commonly used bio-orthogonal chemistries.

COLL 446

Millisecond reaction kinetics between colored anionic complex and cationic polyelectrolytes with varying structure using stopped flow UV/Vis spectrophotometry

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The cooperative binding of toluidine blue (I) + polyethylenesulfonate (A) complex and cationic polyelectrolytes (C) with different composition were studied with stopped flow mixer complemented with a diode array spectrophotometer (wavelength range from 190 nm to 720 nm). The millisecond reaction kinetics of cationic and polyelectrolyte

complexes were studied with the help of the well-known metachromatic effect of toluidine blue. Our goal was to determine the reaction constants for the reactions: $A+C=AC$ and $AI+C=AC+I$. (The reaction $A+I=AI$ is exceedingly fast, in the order of $10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$.) The results can be used in a wide range of applications, including water treatment systems and polyelectrolyte titrations. The kinetics also allows for better characterization of polyelectrolyte interactions and design of polyelectrolyte complexes.

COLL 447

Vibrational sum frequency generation analysis of amine-terminated organosilane self-assembled monolayers

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Self-assembled monolayer (SAM) thin films formed by amine-terminated organosilanes have found widespread use in biosensing devices due to their ease of preparation and their modifiable surface chemistry. Ideally the silane anchors to the surface of a silicon wafer or substrate generating an amine-rich interfacial layer for the attachment of biomolecules. The formation of SAMs is however a very complex process, with extreme sensitivity to preparation conditions such as concentration, temperature, solvent, and deposition time, that can easily result in a non-idealized film structure. We utilize vibrational sum frequency generation (VSFG) spectroscopy to study the interface-specific chemistry of SAMs generated from a variety of amino-terminated organosilanes in an effort to understand and optimize SAM morphology.

COLL 448

Microfluidics: Effect of channel width and design on miscible and partially miscible systems

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Our primary objective was to design and build a microfluidic device in which we could study miscible and partially miscible systems and measure interfacial tension. In this study, we observed how different channel widths and different junctions can affect different miscible and partially miscible systems. We used four different kinds of miscible and partially miscible systems. We used channel widths between 5 to 100 microns and a three-channel joint that merged with different shapes. Junctions that narrowed at different angles had different behaviors. For example, junctions that narrowed and then widened to a S-shaped curve were more likely to have droplet break-up. Too small or too large channel widths had globs of drops or streams that would break up other streams or globs into smaller streams or globs. We conclude that

channel width and junctions can affect the behavior of different types of miscible and partially miscible systems.

COLL 450

Heavy Metal Separation: Could there be a silver bullet?

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Development of a simple metal ion separation method will be discussed, where precipitation chemistry will be utilized. Recently, there have been concerns about the fate of separated wastes. Separation methods that can separate the waste into useful materials can be the answer to these concerns. When designing such a separation method, much attention was paid, so that the separated materials can served some useful purposes. As representative metal ion solutions, Cu^{2+} and Co^{2+} where treated, and the results of these studies will be presented

COLL 451

Perforated Microcapsules with Selective Permeability created by Double-Emulsion Templates

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We report a new microfluidic emulsification technique for production of double-emulsion drops with an ultra-thin middle layer. The ultra-thin shell provides high degree of confinement of the core drops due to strong lubrication resistance along whole interfaces of the shell, making the double-emulsion drops highly stable. Therefore, by employing such double-emulsion drops as templates, we can readily produce microcapsules with ultra-thin membrane without rupture of the templates. In particular, the membranes can be perforated with regular nanopores, thereby providing selective permeability. To produce the perforated membrane, we have employed microphase separation of polymer blends or block-copolymers. Interaction parameter between polymers and their molecular weight determine the size of pore on the membrane; we can control the size of pores in a range of a few nanometers to hundred nanometers. The capsules with the tailored pores are potentially useful for controlled release of encapsulants, separation of catalytic reactions, and immunoisolation.

COLL 452

Microfluidic generation of all-aqueous emulsions

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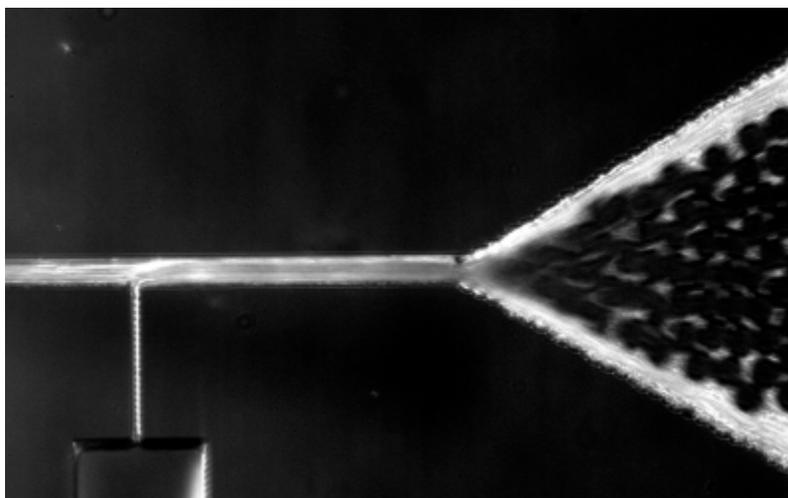
Droplet-based microfluidics have enabled generation of oil-water-based emulsions of tunable size and structure. Besides their direct use, these emulsions also form excellent templates for functional particles, capsules and vesicles, which have demonstrated excellent potential for biomedical applications, such as encapsulation of biomolecules and cells. However, the use of oil-based solvents in the emulsion fabrication process necessitates tedious procedures for their complete removal before the resultant materials can be used in aqueous environments, for instance, in cell culture studies. To address this, all-aqueous emulsions, which are emulsions with dispersed and continuous phases of immiscible aqueous phases, have been proposed as an alternative. The different interfacial and rheological properties of these emulsion phases demand novel emulsion generation and stabilization strategies. In this talk, we will discuss various approaches for preparing all-aqueous emulsions in microfluidic devices and suggest ways to stabilize them.

COLL 453

Foam Structures Using Smectic Liquid Crystals Generated by Microfluidic Device

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Smectic foam is a dispersion of air bubbles in smectic liquid crystal host. The orientational order and the layer structures in smectic liquid crystal effectively stabilize foam structures up to a high air content. The wall separating air bubbles can be a few molecular layers thick. We developed T-shaped microfluidic devices that inject 15 micron meter diameter air bubbles in the liquid crystal at a rate as high as 220 ea/s.



The stability of generated foam is strongly dependent on the phase of the liquid crystal host (isotropic << nematic < smectic). Draining the host liquid crystal results in thinner walls and faceted 3D arrangement of air bubbles. We will report the results of observation of the structural evolution and the changes of optical, mechanical and thermal properties of the foam. The future application of the smectic foam will also be discussed.

COLL 454

Controllable Microfluidic Production of Multicomponent Multiple Emulsions for Engineering Multicompartment Materials

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A hierarchical and scalable microfluidic device constructed from a combination of three building blocks, which are a drop maker, a connector and a liquid extractor, has been developed for highly-controlled generation of multicomponent multiple emulsions. The number, ratio and size of droplets, each with distinct contents being independently co-encapsulated in the same level, can be precisely controlled. Combinations of the building blocks enable scale-up of the device to create higher-order multicomponent multiple emulsions with exceptionally diverse structures. These multicomponent multiple emulsions offer a versatile and promising platform for precise encapsulation of incompatible actives for synergistic delivery and chemical reactions, and for engineering multicompartment materials with controlled internal phases. One of these applications is demonstrated by template synthesis of thermo-responsive multicompartment microcapsules from quadruple-component double emulsions, for co-encapsulation and controlled release of different lipophilic components. This approach brings a significant

breakthrough for the fabrication and applications of controllable multicomponent multiple emulsions.

COLL 455

Stokes flow past a Janus droplet

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Creation by microfluidics of Janus droplets is a precise method to build identical blocks, which can then be used in the design of smart materials, sensors, and catalytic motors. However, most studies in this field are experimental, thus a theoretical analysis of simplest problems is needed. In this talk, we consider a Janus droplet—a compound drop composed of two hemispherical domains occupied by different fluids—in an external flow. The flow is assumed slow in order to neglect both nonlinear effects and deformation of the interfaces. Both analytical solution and numerical computations are performed. First, the conditions of Janus droplet creation are discussed. The shape of a compound droplet is calculated under the following conditions: the surface tension coefficients between each droplet fluid and the ambient are almost equal and larger than the surface tension at the internal interface. Under these conditions the droplet shape is close to the spherical with a flat interface; therefore the droplet comprises two hemispherical domains of different liquids. The motion of such a droplet is analyzed for two particular situations: (i) under uniform flow far from the droplet and (ii) rotation of the droplet under the fixed torque in a quiescent fluid. In case (i) the stable state is found: the droplet is oriented in such a way that the internal interface is perpendicular to the flow and the fluid at the upstream face is less viscous. The Stokes force is found; in most practically relevant cases it is larger than the Hadamard-Rybczynski force imposed onto the drop of the mean viscosity. The torque applied to the droplet beyond the equilibrium state is calculated. In combination with case (ii) this allows calculating the time the droplet needs to reach the equilibrium state.

COLL 456

Encapsulation of polystyrene colloidal particles within a pH sensitive capsule membrane using Microfluidic technique

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We encapsulate surface modified colloidal polystyrene particles (1 μm) within a pH sensitive capsule membrane using microfluidic technique. The capsule membrane consists of a combination of a pH sensitive polymer and a crosslinked

acrylic network. We use different ratio of pH sensitive polymer in the main matrix. Upon exposing pH sensitive capsules to pH gradient, the pH sensitive segments embedded within the main matrix are selectively removed and pores are formed at the membrane surface, subsequently the release of the polystyrene particles can be triggered upon pore formation. In addition, different ratio of pH sensitive polymer in main matrix results in stark contrast between the membrane structure. We observe a close pack arrangement of colloidal acrylate polymer within a pH sensitive polymer matrix at high ratios, while decreasing the ratio results in isolated pH sensitive segments within the main membrane.

COLL 457

Hydrodynamic cavitation: a bottom-up approach to liquid aeration

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We report the use of hydrodynamic cavitation as a novel, bottom-up method for continuous creation of foams comprising of air microbubbles in aqueous systems containing surface active ingredients, like proteins or particles. The hydrodynamic cavitation was created using a converging–diverging nozzle. The air bubble size obtained using this technique was found to be significantly smaller than that achieved using conventional mechanical entrapment of air via shearing or shaking routes, which are in essence top-down approaches. In addition, the technique provided the possibility of forming non-spherical bubbles due to the high elongational stresses experienced by the bubbles as they flow through the nozzle throat. We show that surface active agents with a high surface elasticity modulus can be used to stabilize the nascent air bubbles and keep their elongated shapes for prolonged periods of time. This combination of the cavitation process with appropriate surface active agents offers an opportunity for creating bubbles smaller than 10 microns, which can provide unique benefits in various applications.

COLL 458

Crystallinity and internal structure of photonic balls prepared by colloidal crystallization in the confinement of an emulsion droplet

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We apply microfluidics to prepare emulsions of an aqueous colloidal dispersion in a non-polar continuous phase. If the emulsion is heated, diffusion of water eventually leads to solidification of the colloidal dispersion that can form either amorphous, disordered solids or crystallize into ordered colloidal crystals with a spherical morphology, usually termed photonic balls. If crystalline in nature, these balls show

structural color and can therefore be applied as dispersible coloration agents. We investigate the formation process with emphasis on the effects of the spherical confinement on the resulting structure for photonic balls consisting of direct opals and their inverse analogues prepared from co-assembly of polymer colloids in the presence of small silica particles. We furthermore resolve the internal structure by focused ion beam assisted sectioning of individual, micron-sized objects and correlate their internal structure with their optical properties on a single particle level.

COLL 459

Analysis of foam stability using microfluidic channels

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We utilize a microfluidic constriction to demonstrate two new mechanisms of in-situ foam generation in porous media. The initial foam is generated via a flow-focusing geometry with co-flowing gas and surfactant solution streams, and is then flowed through a microfluidic constriction. By varying the gas and surfactant solution flow rates, different types of monodisperse foam are generated, such that spanning the channel width are two bubbles (2-bubble foam), three bubbles (3-bubble foam), or more than three bubbles (> 3-bubble foam). It is expected that bubbles would snap-off when flowed through the constriction, but snap-off only occurs in our system under unstable conditions, when the foam is wet with a large bubble size. Instead, the following behaviors are observed as the stable foam passes through the constriction: no change, reorientation, and pinch-off via two newly observed mechanisms: neighbor-wall and neighbor-neighbor. Neighbor-wall pinch-off occurs as a bubble is pinched between the surfaces of a neighboring bubble and the curved wall of the constriction.

COLL 460

Microfluidic design of gel microparticles for drug delivery to the lungs

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We are developing a passive targeting approach for drug delivery to the lungs via the venous blood stream. The lung receives the entire venous blood supply from the heart and passes it through the capillary beds on the alveoli. Large particles in the venous blood are thus trapped in these capillary beds. This filtering phenomenon can be used to selectively deliver particles to the lung. Such delivery methods have been safely employed in pulmonary perfusion diagnostic agents; however the use of this novel delivery route for chemotherapeutic drugs has not been appreciated or utilized by the drug delivery community.

The key element of the delivery is precise control of the gel particle size and modulus. The gel microparticles are made by an emulsion process using microfluidics to create droplets of macromers and therapeutic nanoparticles. Polymerization of the 10-40 micron droplet entraps the nanoparticles, but biodegradable lactides in the gel structure degrade in a controlled way to release the drugs. Issues in microfluidic production of highly loaded drops, polymerization, and characterization of gel properties of these microparticles will be discussed..

COLL 461

Crystallization-driven self-assembly of elongated block copolymer micelles

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Elongated micelles with a semicrystalline core are different from traditional cylindrical surfactant or block copolymer micelles. They are stiff and often rod-like. Their growth is irreversible and, if properly nucleated, they can form micelles of controlled and uniform length. When subjected to shear, they fragment, and the fragments do not readily combine. The core typically has domains characterized by different degrees of crystallization. Segments of these micelles dissolve at different temperatures, reflecting the degree of crystal perfection in each segment. Thus the concept of a critical micelle temperature (CMT) or concentration (CMC) is no longer appropriate. My talk will describe these features for examples reported in the literature by other groups as well as several examples from our laboratory.

COLL 462

Polymerization-induced self-assembly

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Methacrylic diblock copolymers are prepared using reversible addition-fragmentation chain transfer (RAFT) chemistry at 70°C using an aqueous dispersion polymerization formulation. The first block is water-soluble poly(glycerol monomethacrylate), whereas the second block comprises water-insoluble poly(2-hydroxypropyl methacrylate). As it grows, the latter block becomes increasingly hydrophobic, which drives *in situ* self-assembly to form spherical nanoparticles of 25-100 nm diameter at 10% solids. Adjusting the copolymer curvature enables the morphology to be varied systematically from spheres to worms to vesicles. Phase diagrams are elucidated, which allows the reproducible synthesis of nanoparticles with predictable morphologies at up to 25% solids. If vesicles are targeted, the block copolymer morphology evolves from spheres to worms to vesicles during the polymerization. TEM studies reveal *jelly-fish* nano-

structures that provide mechanistic insights regarding the worm-to-vesicle transition. The worm phase leads to shear-thinning, free-standing gels at 20°C but degelation occurs on cooling to 5°C due to a reversible worm-to-sphere transition.

COLL 463

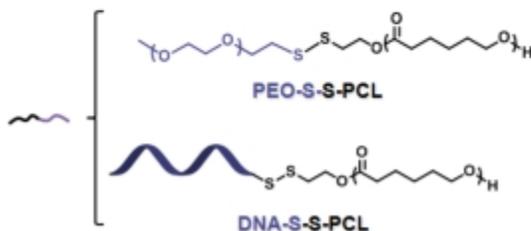
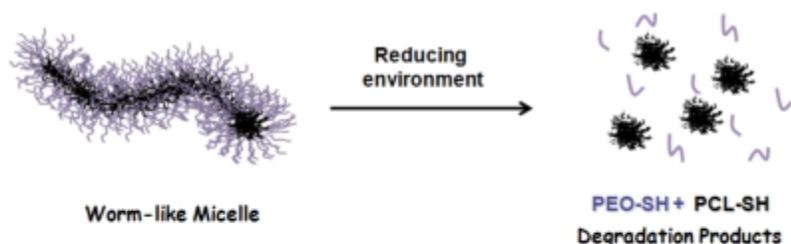
Reductive degradation of poly(ethylene oxide)-S-S-poly(ϵ -caprolactone) assemblies for drug and siRNA delivery

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Worm-like micelles from amphiphilic diblock copolymers represent a very attractive structure for drug delivery due to both high drug loading per carrier and longer in vivo circulation times compared to spherical assemblies.^[1,2] By introducing functionalities in the block copolymer responsive to disease environments the performance of such systems can be in principle enhanced. Here, we describe a diblock copolymer containing a disulfide group connecting both blocks of poly(ethylene oxide)-S-S-poly(ϵ -caprolactone), or PEO-S-S-PCL which self-assembles into worm-like micelles and undergoes degradation under reducing conditions. Further applications of such assemblies would include the delivery of siRNA by incorporating an oligonucleotide-S-S-PCL block copolymer in the assembly. The applicability of such a drug-delivery vehicle is significantly broadened by such responsive functionality.

[1] D. A. Christian, S. Cai, O. B. Garbuzenko, T. Harada, A. L. Zajac, T. Minko, D. E. Discher, *Mol. Pharm.* 6: 1343-1352 (2009).

[2] S.M. Loverde, M.L. Klein, D.E. Discher. *Adv. Mat.* 24: 3823-3830 (2012).



COLL 464

On the phase behavior of polymer micelles having semi-crystalline cores

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Interest in the use of poly(ethylene glycol-*b*-caprolactone) diblock copolymers for thermally triggered drug delivery has led to this study of the phase behavior of polymer micelles made from these diblocks. In aqueous solutions at concentrations above the critical micelle concentration (CMC), the polymer molecules assemble into micelles. Melting endotherms were observed in the DSC of the micelle solutions, indicating the polycaprolactone core was semi-crystalline. The degree of crystallinity depended on the methods used to prepare the polymer micelles. Furthermore, the degree of crystallinity depended on the degree of polymerization for the polycaprolactone block. The CMC slightly increased with increasing temperature as expected due to entropic effects. At temperatures above the melting point of the polycaprolactone core, there was greater increase in the CMC with increasing temperature. Dynamic light scattering showed the hydrodynamic diameter was independent of temperature, confirming that the micelles remained intact when the polycaprolactone core had melted.

COLL 465

F108-templated formation of ultralarge-pore mesoporous silicas with spherical pores

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Ultralarge-pore mesoporous silicas with spherical pores were synthesized by adopting commercially available Pluronic F108 (PEO₁₃₃PPO₅₀PEO₁₃₃) block copolymer surfactant as the template and using judiciously selected swelling agents. FDU-12 silica with face-centered cubic structure (*Fm3m* symmetry) and with unit-cell parameter up to ~51 nm was obtained. Calcined silicas had unit-cell parameters up to ~48 nm and pore diameters up to ~22 nm. The pore size and pore accessibility was controlled by adjusting temperature of the hydrothermal treatment. Interestingly, hollow spherical particles were formed by decreasing the precursor/surfactant ratio. By controlling synthetic conditions, such as using different swelling agents, the size of uniform spherical particles can be tuned from 15 nm to 28 nm.

COLL 466

Hydrophobic Molecules Infiltrating into the PEG Domain of the Core/Shell Interface of a Polymeric Micelle

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The hydrophobic compound tetrabromocatechol (TBC) was chosen as a drug-equivalent model molecule. The bromine atoms in TBC act as probes in anomalous small-angle X-ray scattering (ASAXS) allowing for its localization in the polymeric micelles whose shape and size were determined by normal small-angle X-ray scattering (SAXS). Light scattering measurements coupled with field flow fractionation were also carried out to determine the aggregation number of micelles. A core-corona spherical model was used to explain the shape of the micelles while the distribution of bromine atoms was explained with a rigid spherehard-sphere model. Interestingly, the radius of the spherical region populated with bromine atoms was larger than the one of the sphere corresponding to the hydrophobic core of the micelle. This result suggests that the TBC molecules infiltrate the PEG hydrophilic domain in the vicinity of the core/shell interface.

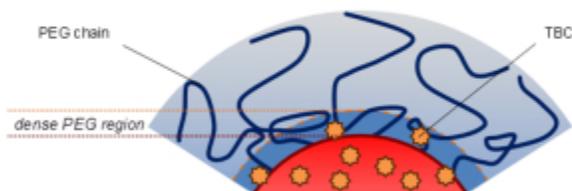


Figure 1 . Schematic picture of the interface of the core, the red region represent the hydrophobic core, blue lines represent PEG chains, and orange polygons represent

COLL 467

Aqueous phase synthesis and characterization of mesoporous zirconia templated by block copolymer and their bioconjugate micelles

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Mesoporous zirconia has attracted great research interest due to its unique properties such as high surface area, uniform pore size distribution, and large pore volume. Self-assembled structures have been used as directing agents to synthesize mesoporous zirconia. Here, we investigate the use of self-assembling block copolymers conjugated to cationic biomolecule lysozyme, as well as self-assembling cationic block copolymers as templates for synthesis of mesoporous zirconia in completely aqueous media. The synthesis of mesoporous zirconia in completely aqueous media with biomolecules will open up opportunities for different mechanisms for controlling zirconia synthesis. The inorganic content of the nanocomposite was determined by TGA, while the structure and composition of the samples was characterized by XRD, nitrogen adsorption, TEM, SEM, SANS, and solid state NMR. The results showed that zirconia nanocrystals formed after calcination of the as-synthesized nanocomposite at 500 °C, and significant crystal growth was observed only after 900 °C calcination. The conjugate-templated zirconia showed a surface area of 174 m²/g after calcination at 500 °C, and retained its tetragonal structure even after calcining at 900 °C. The cationic pentablock copolymer-templated zirconia showed a surface area of 191 m²/g, after calcination at 500 °C, and also demonstrated improved thermal stability. Several parameters such as pH, zirconium ion concentration, and calcination temperature were studied for the block copolymer-lysozyme conjugate template. We found that a more dilute precursor solution and high aging pH would lead to more thermally stable and smaller particles with higher surface area. The 500 °C calcinated zirconia with 0.08 M precursor had the highest surface area of 348 m²/g.

COLL 468

Micelles by Pluronic poly(ethylene oxide)-poly(propylene oxide) block copolymers: Model systems with many applications!

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Block copolymers of the poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) family, commercially available as Pluronics or Poloxamers, offer prime examples of self-

assembling systems that are being explored for diverse applications, ranging from drug delivery carriers to electrolytes for lithium batteries. The presentation will utilize research findings from our group and others to highlight (i) fundamental aspects of Pluronic block copolymer micellization in selective solvents [1-5], and (ii) applications of Pluronic micelles in solubilization [6], surface modification [7], colloidal dispersion [8], nanoparticle synthesis [9], and nanoparticle organization [10].

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COLL 469

Membrane lipid composition regulates the conformation and activity of the antimicrobial peptide maculatin 1.1

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Mastering the structure-activity relationship and specificity of antimicrobial peptides (AMP) against bacterial lipid membranes is required for the therapeutic development of membrane-active peptides. The affinity for a particular lipid composition is often assumed to be the regulative mechanism, but AMP often attack charged membranes mimicking the bacterial envelope almost as efficiently as neutral and cholesterol-containing membranes mimicking eukaryotic cells. For instance, maculatin 1.1 is a 21 residue cationic AMP secreted from the skin of Australian tree frogs that acts against Gram positive bacteria but also has appreciable haemolytic activity. The peptide secondary structure was determined by CD spectroscopy in unilamellar vesicles and oriented bilayers using a range of phospholipids and was strongly influenced by lipid

chain length and saturation. Dye release experiments using binary lipid mixtures in a competitive environment were performed to determine the AMP mechanism and affinity towards a particular lipid composition. The results indicate that a distinct structure of maculatin 1.1 is not essential for lytic activity and support a pore mechanism which is regulated by the membrane lipid composition.

COLL 470

Re-orientation, dimerization and translocation of the membrane-bound antimicrobial peptide PGLa from microsecond all-atom MD simulations

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The membrane-active antimicrobial peptide PGLa from *X. laevis* is known from solid-state ²H-, ¹⁵N- and ¹⁹F-NMR spectroscopy to occupy two distinct α -helical surface adsorbed states in membranes: a surface-bound S-state with a tilt angle of $\sim 95^\circ$ at low peptide-to-lipid molar ratio (P/L = 1:200), and an obliquely tilted T-state with a tilt angle of 127° at higher peptide concentration (P/L = 1:50). Tilt and azimuthal rotation angles calculated from μ s-scale molecular dynamics simulations suggest that the S-state is monomeric, while the T-state consists of a stable antiparallel dimer. Assembly of multiple dimers into higher oligomeric aggregates, or the formation of pores, is not observed during long-scale simulations performed on the ANTON supercomputer at P/L=1:36. Instead we report the first computational description on the membrane translocation mechanism of a highly charged (+5) cationic peptide without the formation of multimeric pores.

COLL 471

Electrical response of lipid bilayers to the bee venom toxin melittin using electrochemical impedance spectroscopy

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Melittin is an interfacially active α -helix that causes membrane destabilization via a mechanism that is still disputed. While a transmembrane pore model has been a central part of the mechanistic dialogue for decades, there is growing evidence that a transmembrane pore is not required for melittin activity. In part, the controversy is due to limited experimental tools to probe the bilayer's response to melittin. Electrochemical

impedance spectroscopy (EIS) is a technique that can reveal details of molecular mechanism of peptide activity, as it yields direct measurements of membrane resistance and capacitance of supported bilayers. In the work presented here, this technique was used to study the response of surface-supported bilayers of different lipid compositions to melittin. The EIS results directly demonstrate that the interfacial response of a bilayer to melittin cannot be explained by a simple transmembrane pore model.

COLL 472

Antimicrobial, cytolytic, and cell-penetrating peptides: Graded and all-or-none release, translocation, and mechanism in model membranes

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We tested the hypothesis that membrane-active peptides can translocate across the lipid bilayer if their Gibbs energy of insertion from the membrane interface is below a certain threshold, and that those peptides should induce graded release from vesicles. We found that all-or-none release indicates that peptides do not translocate, but graded release is not sufficient to conclude they translocate. For cell-penetrating peptide variants the Gibbs energy of transfer to the bilayer interior (transfer from water to bilayer interface and from the interface to the membrane interior) was a good indicator of activity and probably of translocation. But for cytolytic and antimicrobial peptides, the best indicator of activity is the Gibbs energy of binding, suggesting their mechanism does not involve translocation. Finally, the relation between dye release and translocation in GUVs was examined. It is consistent with the results in LUVs and with the hypothesis on the thermodynamic basis of translocation.

COLL 473

pH Dependant Electrostatic Interactions of Antimicrobial Peptides

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We recently described a family of cationic antimicrobial peptides (cAMPs) selected from a combinatorial library that exhibited potent, broad spectrum activity at neutral pH and low ionic strength. To further delimit the utility and activity profiles of these peptides, we investigated the effects of solution conditions such as pH and ionic strength on the efficacy of the peptide antimicrobials against a panel of microorganisms. Peptide minimum sterilizing concentrations (MSC's) varied linearly with pH for each subtype within our family of cAMPs for all organisms tested. The peptides were much less effective against Gram negative bacteria at high pH, consistent with a decrease in net positive charge on the peptides. Surprisingly, the opposite pH trend was observed with the Gram positive *Staphylococcus aureus*. The novel species specific effects of pH observed here have important implications for the use of cAMPs in a clinical setting.

COLL 474

Pore formation in DMPC bilayers by antimicrobial peptide melittin: Mathematical model and comparison with experiments

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Pore formation in DMPC bilayers by antimicrobial peptide melittin as monitored by leakage of fluorescent dyes (calcein, FD4 and FD20) of different molecular weights encapsulated within liposomes indicated a lagtime which was larger for smaller melittin liposome ratio and larger molecular weight of dye. Pore formation was also demonstrated through direct observation of dye leakage using confocal microscopy. Circular dichroism of melittin showed an increase in α helical conformation when exposed to liposome. Observed timelag for deactivation of *listeria monocytogenes* by melittin as monitored by absorbance and plate count was found to be concentration dependent. A mathematical model for the prediction of time of pore formation was proposed accounting for (i) adsorption of melittin onto bilayer (ii) surface aggregation and (iii) energy barrier for formation of hydrophobic (barrel stave mechanism) or hydrophilic (toroidal mechanism) pores. Model predictions showed the mechanism for pore formation to be toroidal and agreed with experiments.

COLL 475

Structural changes and stability of oxidized lipid monolayers: Insight from atomistic molecular dynamics simulations

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Lipid-containing surfactant films on ocean and lake surfaces as well as on aqueous atmospheric aerosols affect a wide range of important processes, from water evaporation and condensation to light scattering to heterogeneous chemistry. It is commonly assumed that atmospheric oxidation, leading to polar products, increases the hydrophilicity of lipid coatings and results in higher water uptake. Using molecular dynamics (MD) simulations, we studied Langmuir monolayers of phospholipids, fatty acids and long-chain alcohols to obtain atomistic level insight into the intermolecular interactions and structural characteristics as a function of surface density, and to study the changes triggered by oxidation. MD simulations reveal that structural changes in the monolayer depend on the spatial density of oxidized functional groups, and may include effects such as transient accumulation of volatile oxidation products or orientational reversal of oxidized chains. Implications for the hydrophilicity of oxidized lipid films will be discussed.

COLL 476

Total Internal Reflection Raman Spectroscopy of Organic Films at Solid-Water Interfaces

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Total internal reflection Raman spectroscopy exploits the limited penetration depth of an evanescent wave to probe thin films at buried interfaces with chemical selectivity. Current technology has a sensitivity limit of 1% of a monolayer, a time resolution of 1 s and the ability to discriminate at least three different chemical species even with heavily overlapped spectra. Examples will be presented for the adsorption of pure and mixed surfactant systems at the silica-water interface. The range of substrates can be extended by deposition of a thin film of the material of interest onto an optically transparent substrate. This approach will be illustrated by adsorption of surfactants onto cellulose from aqueous solutions.

COLL 477

Surface structure of polyethylenimine thin films as a function of relative humidity analyzed with vibrational sum frequency spectroscopy

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Reactive or self-decontaminating polymer materials that provide protection against chemical or biological weapons are of fervent interest to the Department of Defense. Polyethylenimines (PEI) have found broad use in current self-decontaminating platform technologies due to the high density of reactive amine groups. Furthermore, PEI materials are utilized in a wide array of additional applications, including gene transfection and chemical/biological sensing, that depend heavily upon the surface functionality and morphology of the materials. It is therefore critical to understand the surface-specific interactions occurring at the interface in order to systematically enhance the performance of future polymer-based self-decontaminating platform materials. To this end we utilize vibrational sum frequency generation spectroscopy (VSFG) to study the interfacial behavior of linear and branched polyethylenimine thin films as a function of their chemical environment. We observe the PEI film surface structure to be highly responsive to changes in relative humidity.

COLL 478

Air-aqueous interfaces, ion distributions, and lipid organization by vibrational sum frequency generation spectroscopy

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Motivated by atmospheric aerosol chemistry of marine and urban regions, ocean surface chemistry, and vadose zone interfacial exchange/reactivity, monovalent and divalent cations and anions were investigated using phase sensitive sum frequency generation (PS-SFG) spectroscopy to understand the surface propensity and availability for reaction at water surfaces. Ion valency, polarizability, size, shape, and identity of the counterion are critical factors in considering ion organization at the air water interface. Phospholipids and fatty acids were also studied using both SFG and Brewster angle imaging. Head group differences, especially with regard to hydrogen bonding capability and extent, are discerning factors for surface organization and shape distinction at the water surface.

COLL 479

Molecular insight into the preferential adsorption of monovalent ions to selected polar surfaces: a vibrational sum frequency spectroscopy study.

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Vibrational Sum Frequency Spectroscopy (VSFS) has been used to study the preferential adsorption of a series of ions to charged and uncharged fatty acid monolayers. Ion enrichment is determined indirectly by targeting surface water vibrational modes. Interfacial water molecules are affected by the presence of ions in mainly two distinct ways. First, their hydrogen bond strength, coordination, and orientation are modified when locally participating in the ion hydration shells. Second, surface electric fields generated by non-monotonic ion profiles induce a preferential orientation of the water dipoles that may extend several molecular layers. VSFS proves to be highly sensitive to both such cases. Ions were classified depending on their propensity to adsorb to both interfaces which appear to follow the Hofmeister series.

COLL 480

The assembly of emulsion stabilizing molecular agents using vibrational sum frequency scattering spectroscopy

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Emulsions made up of oil/water mixtures are of universal importance in the food and cosmetic industries as well as water remediation technologies. Often what governs the properties of an emulsion is the molecular agent (i.e. polymers, surfactants, or nanoparticles), which stabilizes the interface between the oil and water phases. It is, therefore, necessary to understand how these molecular agents affect the molecular structure and hydrophobicity in stabilizing emulsions. This presentation will report our studies of nanoparticles and surfactants with emphasis on the disorder of alkyl chains

by monitoring the C-H modes as a function of various parameters, such as pH and size using vibrational sum frequency scattering spectroscopy.

COLL 481

Effects of Molecular Size and Surface Hydrophobicity on Oligonucleotide Interfacial Dynamics

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Single-molecule total internal reflection fluorescence microscopy was used to observe the dynamic behavior of (poly)-cytosine ssDNA (1-50 nucleotides long) at the interface between aqueous solution and hydrophilic (oligoethylene oxide-modified fused silica, OEG) and hydrophobic (octadecyltriethoxysilane-modified fused silica, OTES) solid surfaces. High throughput molecular tracking was used to determine >75,000 molecular trajectories for each molecular length, which were then used to calculate surface residence time and squared displacement (i.e. "step-size") distributions. On hydrophilic OEG surfaces, the surface residence time increased systematically with ssDNA chain length, as expected due to increasing molecule-surface interactions. Interestingly, the residence time decreased with increasing ssDNA length on the hydrophobic OTES surface, particularly for longer chains. Similarly, the interfacial mobility of polynucleotides slowed with increasing chain length on OEG, but became faster on OTES. On OTES surfaces, the rates associated with desorption and surface diffusion exhibited the distinctive anomalous temperature dependence that is characteristic of hydrophobic interactions for short chain species but not for longer chains. These combined observations suggest that long oligonucleotides adopt conformations minimizing hydrophobic interactions.

COLL 482

Hydrophobically Modified Biopolymer as enhanced carrier for in situ groundwater remediation

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Carbon submicrospheres as a carrier for nanoscale zerovalent iron particles are of much potential in the remediation of chlorinated compounds. Effective in situ groundwater remediation requires the successful delivery of these reactive systems through soil without aggregation. Here, we show that hydrophobically modified chitosan(HMC), with C12 alkyl groups stabilize carbon submicrospheres through hydrophobic interactions. Detailed NMR characterizations indicate attachment of the alkyl

groups onto the microspheres. The coating of the environmentally benign biopolymer therefore leads to suspension stability of these submicrospheres through electrostatic and steric repulsion. Compared with pristine chitosan and commonly used sodium carboxymethyl cellulose (CMC), HMC is more effective in stabilizing carbon submicrospheres, and this is even enhanced under normal groundwater iron strength condition. Our results indicate that this system has optimal transport characteristics in groundwater saturated sediments with carbon submicrospheres attachment efficiency of 0.04 calculated from breakthrough data of capillary transport experiments. The fundamental concepts will be detailed in the talk.

COLL 483

Novel in situ techniques for studies of model catalysts

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Motivated mainly by catalysis, gas-surface interaction between single crystal surfaces and molecules has been studied for decades. Most of these studies have been performed in well-controlled environments, and has been instrumental for the present day understanding of catalysis. We have in recent years explored the possibilities to perform experiments at conditions closer to those of a technical catalyst, in particular at increased pressures. In this contribution, results from catalytic CO oxidation over Pd and Rh single crystal surfaces using High Pressure X-ray Photo emission Spectroscopy (HPXPS), Planar Laser Induced Fluorescence (PLIF), and High Energy Surface X-Ray Diffraction (HESXRD) will be presented.

Armed with structural knowledge from ultra-high vacuum experiments, the presence of adsorbed molecules and gas-phase induced structures can be identified, and related to changes in the reactivity and/or to reaction induced gas-flow limitations. The strength and weaknesses of the experimental techniques will be discussed.

COLL 484

In Situ Studies of Surface Chemical Reactions: From Simple Molecules to Porphyrins

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Chemical reactions on surfaces can be followed in detail using X-ray photoelectron spectroscopy (XPS or ESCA). From the binding energies of the adsorbate and substrate core levels, detailed information not only on the chemical composition, chemical state (e.g. oxidation state) and adsorption sites, but also on the vibronic final state in the photoemission process itself can be derived. In this presentation, two examples will be addressed. The first deals with the adsorption of saturated and

unsaturated hydrocarbons on metal surfaces. From high resolution XP spectra, obtained at BESSY-II, detailed information on the adsorption, dissociation and the formation of new species, including graphene, can be derived. The vibrational fine structure of the XP spectra is analyzed in detail and can be used to identify various surface intermediates. The second example addresses the adsorption of metalloporphyrins on metal surfaces. In particular we will discuss the synthesis of metalloporphyrin monolayers by direct metalation of porphyrin monolayers.

COLL 485

Alkane activation by oxides doped with high-valence dopants

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I will discuss catalysis by oxides that are substitutionally doped with cations whose valence is higher than that of the cations they replace in the host oxide. I will show examples of catalytic behavior for three situations. 1. The host oxide is irreducible and the valence of the dopant is not much higher than that of the cation in the host. 2. The host oxide is irreducible and the dopant has much higher valence. 3. The host oxide is reducible. In these situations, doping will activate the breaking of the C-H bond in an alkane but it will do this by different mechanisms. I will also discuss the stability of these systems and the difference between the cases when the host oxide is reducible or irreducible.

COLL 486

Application of Raman spectroscopy for in-situ studies of catalytic biomass conversion

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Raman spectroscopy is a powerful tool for the study of chemistry under reaction conditions. This is particularly true for the aqueous phase conversion of biomass components where water can interfere with other spectroscopic experiments based on infrared spectroscopy and NMR. This presentation will describe recent combined experimental and computational studies applied to the interpretation of Raman spectra from complex molecules and to the catalytic conversion of furfural alcohol an important biomass intermediate.

COLL 487

Oxidative dehydrogenation of ethane on supported chloride catalysts

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A selective route from ethane to ethene is an important goal to improve the carbon footprint of this large volume chemical. The new catalyst system reported comprises of a solid redox-active oxide core and a 2 - 5 nm thick molten alkali chloride overlayer. The alkali chloride overlayer is able to dissolve molecular oxygen. At the solid liquid interface O₂ is dissociated and converted to an active species, which oxidizes ethane at the surface of the molten chloride. Steady state and transient kinetics together with isotope labeling show that the activation of O₂ is rate determining and proceeds via a Mars-van Krevelen type mechanism. A small concentration of active species, presumably hypochlorite anions, at the liquid-gas interface catalyzes the dehydrogenation of ethane. The lecture discusses the catalyst physicochemical properties, the elementary steps for the reaction as well as chances and limitations of the new approach.

COLL 488

Enticing features of oxides and sulfides: Reactivity, selectivity and other functionalities

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Oxide surfaces serve as catalysts either directly or as support for nanoparticles, leading to questions about the role of interface atoms, charge transfer and oxygen vacancies. Motivated by experimental results of high CO oxidation rate on Cu₂O nanoparticles [1], and selectivity in NH₃ oxidation on RuO₂(110) [2], I will present results from density functional theory and kinetic Monte Carlo simulation of the rates of these reactions on respective surfaces. Conclusions will be drawn about features of the surface electronic structure and local environment that may hinder or facilitate a particular reaction. Since reactions may leave oxygen vacancies in the surface, I will address the question of healing of the surface (Cu₂O). For NH₃ oxidation on RuO₂(110), I will elaborate on conditions which may hinder the experimentally observed selectivity of reaction products [3]. I will turn also to recent findings of the novel properties of single and bilayer of MoS₂, particularly on features in the local environment that may lead to notable reactivity of this 2D material.

1. B. White, et al., Nano Letters **6**, 2095 (2006).
2. Y. Wang, et al., J. Phys. Chem. B **109**, 7883 (2005).

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COLL 489

Surface Spectroscopy and Microscopy of Catalytic Reactions

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The performance of heterogeneous catalysts frequently depends on the details of catalyst synthesis, activation and operation. However, in many cases the exact origin of such effects is unknown. The combination of ultrahigh vacuum grown model catalysts with in situ surface analytical methods, that can operate while the catalyst is functioning, may provide definite answers. In this contribution it is shown how surface spectroscopy [1], e.g. by polarization modulation IR spectroscopy or synchrotron based XPS, and surface microscopy by PEEM [2] can be applied to explain the selectivity of alloy catalysts and to monitor the locally-resolved reaction kinetics on polycrystalline surfaces. The model studies are contrasted to corresponding studies of technological catalysts.

[1] Ch. Rameshan, W. Stadlmayr, Ch. Weilach, S. Penner, H. Lorenz, M. Hävecker, R. Blume, T. Rocha, D. Teschner, A. Knop-Gericke, R. Schlögl, N. Memmel, D. Zemlyanov, G. Rupprechter, B. Klötzer, *Angewandte Chemie International Edition*, 49 (2010) 3224-3227.

[2] D. Vogel, Ch. Spiel, Y. Suchorski, A. Trinchero, R. Schlögl, Henrik Grönbeck, G. Rupprechter, *Angewandte Chemie International Edition*, 51 (2012) 10041–10044.

COLL 490

Bonding of ammonia and its dehydrogenated fragments on Ru(0001)

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The catalytic decomposition of ammonia has attracted attention due to its high hydrogen storage capacity and the possibility to produce hydrogen without toxic or greenhouse gases as byproducts, making ammonia a potential candidate for fuel cells. The dehydrogenation reaction is thermally activated and thus requires heating or energy input. Ruthenium is one of the most active catalysts and has been the objective of many experimental and theoretical efforts to calculate dissociation and hydrogenation

mechanisms. In spite of this there is still no consensus on the adsorption sites and geometries of intermediate species, including NH_2 and NH . In this presentation we report scanning tunneling microscopy experiments and density functional theory calculations that unambiguously establish the adsorption sites and the dissociation pathways of ammonia on $\text{Ru}(0001)$. All the N-H bond cleavage reactions were induced by controlled tip manipulation to produce each of the NH_x ($x=0-2$) intermediates.

COLL 491

Field-directed observation of membrane dynamics using supported lipid bilayers

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Artificial models of cell membrane attracts increasing attention because they can be used to study the interactions between a lipid bilayer, the protective envelope of cell membrane, and other small molecules involved in a variety of cellular processes, such as antimicrobial peptides and phospholipase enzyme. Two artificial models have been studied: supported lipid bilayers (SLBs) and giant unilamellar vesicles (GUVs), which are formed through vesicle fusion and electroformation, respectively.

Antimicrobial peptides are involved in the defense system for most of organisms, including humans. These peptides attach onto cell surfaces, and further insert into the membrane, either forming pores or accumulating like a carpet, both of which will cause the cell death. Thus antimicrobial peptides have therapeutic potential as new antibiotics for bacteria that are resistant to common antibiotics. In this study, alamethicin is chosen, because it follows a typical barrel-stave model. Our QCM data shows that the SLBs can be disrupted by alamethicin at 50 μM . This disruption is confirmed by confocal microscope using fluorescent lipids. To better understand the interaction between alamethicin and lipid bilayer, we use microfluidic devices to monitor the interaction between alamethicin and bilayer.

COLL 492

Coupled phase transition phenomena in lipid bilayer membrane systems

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Lipid bilayer membrane systems represent an interesting and important class of soft materials, ranging from supported membranes (in contact with an aqueous solvent) to synthetic vesicles (enveloping homogeneous or heterogeneous liquid phases) to living cells. Due to their structure, the leaflets comprising the bilayer membrane are strongly coupled to their environments and susceptible to thermo-mechanical perturbations. This coupling results in several related intriguing phenomena, such as registration of compositional lipid domains across the two bilayer leaflets in supported membranes or

vesicles, effect of solvent hydrodynamics on critical and coarsening behavior of bilayer membranes, spatial correlation of compositional lipid membrane domains with co-existing bulk phases in giant vesicles, and the formation of dynamic liquid-like protein aggregates within the bulk cytoplasm and their interaction with membrane proteins.

In this talk, I will provide an overview of our on-going studies of coupled phase transition phenomena in lipid membrane systems. In particular, I will discuss the dynamics of compositional lipid domains within symmetric leaflets, and their interaction with an aqueous bulk phase which itself may undergo a demixing transition.

COLL 493

Diffusion of proteins and other objects in lipid bilayer membranes

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We present a numerical scheme to predict the diffusion coefficients of arbitrarily shaped objects embedded in lipid bilayer membranes.

COLL 494

Predictions for Cholesterol Interaction Sites on the A_{2A} Adenosine Receptor

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Molecular dynamics simulations of the A_{2A} adenosine receptor totaling 1.4 μ sec show clear evidence for specific sites mediating interactions between adenosine-bound A_{2A} and cholesterol. The strongest evidence is for three binding sites. Two are in the extracellular leaflet, with one site interacting with helices VII and I, and the other with helices II and III. One site is located in the intracellular leaflet, interacting with helices III and IV. One of our three predicted binding sites is confirmed by a just-published high resolution structure of A_{2A} cocrystallized with an antagonist. [Lee, JY and Lyman, E J. Am. Chem. Soc. 134:16512(2012)]

COLL 495

Supported lipid membranes on graphene oxide and reduced graphene oxide: Effect of the degree of reduction

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Artificial lipid membranes on graphene and its derivatives are attractive sensing platform for biomembranes by applying unique graphene-based techniques such as fluorescence quenching assay and solution-gated FET. We describe the fabrication of planar lipid membranes on graphene oxide (GO) and reduced GO (r-GO) by the vesicle fusion method, and the effect of the degree of the reduction. The GO flakes deposited on SiO₂/Si substrates were reduced with the vapor of hydrazine monohydrate. XPS spectra showed that oxygen components decreased with the reduction time and temperature. The vesicle fusion of zwitterionic dioleoylphosphatidylcholine on GO and r-GO resulted in the formation of double lipid bilayers, single bilayer, adhesive vesicles, monolayer, and bilayer/monolayer stacking structures depending of the reduction degree of r-GO. We also describe the results of fluorescence recovery after photobleaching (FRAP) and single fluorescence molecule tracking of the lipid bilayers on GO to evaluate the membrane fluidity.

COLL 496

Bilayer Asymmetry, Cholesterol Content, and Ligand Binding Influence Membrane Protein Sequestering in Raft-Mimicking Lipid Mixtures

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Lipid heterogeneities play an important role in the distribution and functionality of membrane proteins in the plasma membrane. At the cellular level, the analysis of this functional relationship is complicated, due to the small size and transient character of such heterogeneities. Therefore, we explore the biophysical mechanisms of protein sequestering using a model membrane platform with micron-size raft-mimicking phase separations. By applying single molecule-sensitive confocal fluorescence intensity analysis combined with a photon counting histogram method, we show that bilayer asymmetry, cholesterol content, and ligand binding have a significant influence on the sequestering of integrins. The observed changes in integrin sequestering can be attributed to differences in lipid packing and hydrophobic matching, as well as ligand-induced conformational changes affecting protein-lipid interactions. The regulatory role of ligands in membrane protein sequestering is also demonstrated on GPI-anchored urokinase receptors (uPAR). Here ligand-mediated changes in uPAR sequestering are associated with different receptor dimerization levels.

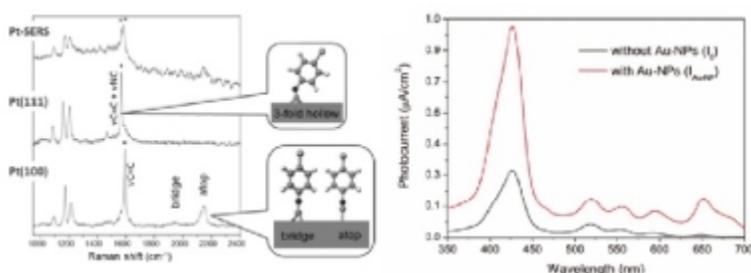
COLL 497

Sphere-plane nanogap structures for enhancement of Raman scattering and photocurrent generation on a chemically modified electrode

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Various electrochemical functions are realized by surface modification of an electrode with functional molecules. Here, we demonstrate that sphere-plane nanogap metal structures can function as optical antennas on a chemically modified electrode; both Raman scattering and photo-induced electron transfers are significantly enhanced on atomically defined single crystalline metal electrodes covered with self-assembled monolayers.

K. Ikeda, K. Uosaki, et al., *J. Phys. Chem. C*, 116, 20806. (2012) / *Angew. Chem. Int. Ed.* 50, 1280 (2011) / *Nano Lett.* 11, 1716 (2011) / *Chem. Phys. Lett.* 460, 205 (2008).



COLL 498

Metallic nanostructures with tunable plasmonic properties

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This presentation will be focused on our recent progress in the fabrication of metallic nanostructures with tunable plasmonic properties by using colloidal synthesis and self-assembly methods. We will first discuss the tailored synthesis and shape evolution studies of plate-like silver nanostructures, with particular emphasis on a unified set of colloidal approaches for the synthesis of silver nanoplates with well-controlled size and shape, high stability, and tunable surface plasmon band from ~400 nm to IR. Second, we will discuss the tuning of the optical properties of metallic nanostructures through manipulating the surface plasmon coupling using a number of self-assembly approaches. In particular, the self-assembly of charged gold nanoparticles into linear chain structures in solution enables a class of dynamically tunable plasmonic structures.

COLL 499

Hybrid Ag – TiO₂ films for surface plasmon enhanced optical absorption and photochemical reactivity

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The growth mechanism of hybrid Ag-TiO₂ films and their morphology and properties are reported using Reactive Layer Assisted Deposition (RLAD) method under ultra high vacuum conditions. The oxide film formation involves Ti atoms deposition on top of amorphous solid water (ASW) condensed on a SiO₂/Si(100) support at 90K. Subsequent annealing leads to desorption of all non-reacted buffer molecules, resulting in deposition of the titanium oxide film. Employing mass spectrometry and using D₂O as buffer, evolution of deuterium molecules has been detected during titanium atoms deposition. A solid state sol-gel-like formation mechanism of titanium oxide is proposed based on these observations. The morphology of the oxide films is characterized by AFM as a rather uniform amorphous thin film at room temperature. Upon annealing above 750K, crystallization of the titanium oxide film has set-in coinciding with a dewetting process of the oxide layer, information obtained from similar growth procedure on amorphous carbon covered TEM grid. Silver nano-crystals grown via ASW as buffer layer were embedded within the titanium oxide layers to form a hybrid metal-oxide film. Enhancement of optical absorption in the visible region due to surface plasmon resonance of the silver particles is reported. The photochemical activity of this hybrid system and its sensitivity to the silver particles size and the number of alternate Ag-TiO_x layers will be discussed.

COLL 500

New synthetic approaches to gold and silver nanostructures with enhanced properties

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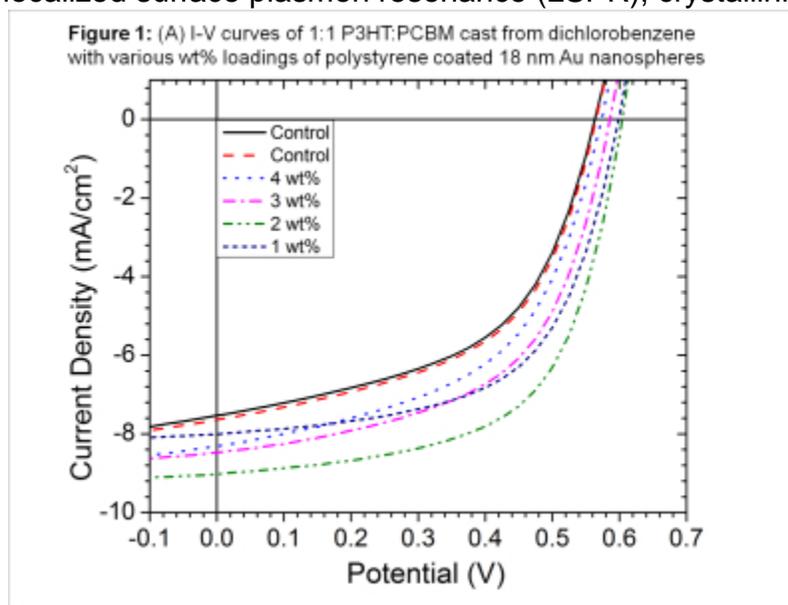
Gold and silver nanostructures are appealing to many researchers in part because of their optical and catalytic applications. While numerous methods for making nanoparticles of these two metals have been developed over the years, there are plenty room for the further development of new synthetic approaches or those methods resulting in nanostructures with new properties. In this presentation, I present results from my group on 1) a new solution phase approach where the reaction can be self-regulated, and 2) new structures that possess much enhanced catalytic, mechanical and optical properties. I will present evidence that the enhanced performance is closely related to the compositions and structures of gold or silver nanocrystals created.

COLL 501

Improved light-harvesting in organic solar cells with plasmonic nanoparticles in the active layer

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We report on progress toward increased light-harvesting ability in P3HT/PCBM bulk heterojunction solar cells as a result of incorporating polystyrene-coated Au nanoparticles into the device active layer. Improvements in power conversion efficiency approaching 30% are observed. We describe efforts to deconvolute the major potential pathways for increased power conversion efficiency, including light scattering (LS), localized surface plasmon resonance (LSPR), crystallinity and morphology changes.



COLL 502

Gold nanomolecules: Gold nanoparticles of molecular definition and size dependent optical properties

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Gold Nanomolecules - molecular gold nanoparticles (<3nm) with a precise number of gold atoms and thiolate ligands - are superstable (air, moisture, temperature 100°C), possess size dependent electronic, electrochemical, chiral properties and can be scaled up in large quantities. Typical examples of nanomolecules include, Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, Au₄₀(SR)₂₄, Au₆₈(SR)₃₄, Au₁₀₂(SR)₄₄, Au₁₄₄(SR)₆₀ and Au_{~300}(SR)_{~90}, where SR is an organic thiolate ligand.

The synthesis, characterization and size dependent optical properties will be discussed.

COLL 503

Organic bulk heterojunction photovoltaic devices incorporating 2D arrays of cuboidal silver nanoparticles: Plasmon enhanced performance

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Photocurrent generation and enhancement by nanoparticles are known to be affected by size, shape, and proximity of neighboring nanoparticles. We assess how plasmonic effects from arrays of cuboidal silver nanoparticles and spheres influence the photocurrent performance of polymer photovoltaic devices incorporating a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as active layer. Nanoparticles were assembled on either tin-oxide (ITO)-coated and silicon glass using the Langmuir Blodgett (LB) technique at different coverage density forming 2D ordered arrays. Our results demonstrate that for solar cell structures with 11.9, % surface coverage, Incident photon-to-photocurrent conversion efficiency (IPCE) is increased by 20 % (from 50% to 70%) whereas efficiency (η) is increased by 24 % from the reference device. Exciton-plasmon interactions through photoluminescence and absorption measurements of the thin-films as a function of particle density and the proximity of neighboring particle are also highlighted.

COLL 504

Light harvesting and electron transport improvements with nanowire arrays incorporated in photovoltaic devices

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Nanoarchitectures may be the key to increasing power conversion efficiencies in photovoltaic devices due to optical and electron transport enhancements. Metal nanowire arrays not only aid in electron transport and photon confinement, but surface plasmon resonance may also increase the light harvesting efficiencies of photovoltaic devices. Template assisted electrochemically grown gold nanowire arrays were incorporated into inverted organic photovoltaic (OPV) devices as high workfunction electrodes. The well aligned radial structures increased the interfacial surface area and decreased the pathlength of excitons in the bulk-heterojunction matrix, thus allowing for thicker devices to be fabricated. Thicker devices are advantageous due to a greater

light harvesting efficiency. Photovoltaic efficiency, electron transport, and optical behavior of these devices will be reported.

COLL 505

Silver and silver-gold bimetallic nanoparticles with various shape, size and surface chemistry: Synthesis, optical and antibacterial properties

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Silver and gold-silver bimetallic nanoparticles find extensive applications in a wide range of areas due to many of their unique properties. The properties of these nanoparticles are highly dependent on the particle attributes like shape, size, aspect ratio, surface chemistry, etc. It is important to understand the relationship between particle property and their attributes in order to design the nanostructures with optimum performance for many of the applications. We synthesized a library of monodisperse silver and silver-gold bimetallic nanoparticles with independent adjustable shape, size and surface chemistry. The optical and antibacterial properties of these particles are investigated. The systematical study of the relationship between nanoparticle property and structure paves the way to nanomaterials by design.

COLL 506

Cellular Backpacks based on Stimuli-Responsive Multilayers

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Cellular Backpacks are nanoscale thick, cargo carrying assemblies that can be attached to a living cell to provide additional function and capability. When synthetic backpacks are attached to immune system cells such as T-cells and phagocytes, the desired cargo is a therapeutic drug that can be released on demand after the cell reaches the disease site of interest. In this talk, strategies for attaching cellular backpacks based on polyelectrolyte multilayers will be discussed including schemes for the covalent attachment of backpacks to living cells. The use of stimuli-response polymers for both fabricating backpacks and on-demand release of drugs from backpacks will be described. In the former case, a detailed characterization of stimuli-responsive hydrogen-bonded multilayers by techniques such as depth profiling XPS will be presented along with suitable design requirements for their use in the fabrication process.

COLL 507

Remote activation of photochemical processes in live cells using colloidal near-infrared-to-ultraviolet nano up-converters

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Near infrared light can penetrate deep into biological tissue, which, therefore, holds promise for remote activation of some particular processes that is far below the skin.¹ However, light-mediated photochemical reactions generally require the use of ultraviolet (UV) or visible light to be initialized. Photon upconversion in rare-earth ions is a step-wise multiphoton process that can efficiently convert two or more NIR photons to produce anti-Stokes emission of a higher energy photon (e.g., NIR, visible, UV) using an inexpensive, low power continuous-wave (cw) diode laser excitation.^{1,2} Using colloidal nanochemistry to nanocontrol of the interfacial processes and excitation dynamics, we show that we are able to produce efficient and selective, visible and UV upconversion emissions in especially engineered upconversion nanoparticles. In particular, utilizing NIR-to-UV upconversion nanoparticles as a UV “nanolamp”, we are able to activate non-fluorescent caged fluorescein to a fluorescent state inside live cells, displaying their applicability for remote biocompatible photoactivation.

Keywords : Photon Upconversion, Remote Activation, Near Infrared

¹P. N. Prasad, “Introduction to Nanomedicine and Nanobioengineering”, Wiley, New Jersey (2012)

²P. N. Prasad, “Nanophotonics”, Wiley, New Jersey (2004)

COLL 508

Remote controlling of micron sized polyelectrolyte capsules

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Polyelectrolyte multilayer capsules represent a unique tool to fabricate micron and submicron sized delivery system with externally guided properties using remote physical stimuli such as light, magnetic field and/or ultrasound. Versatile approach to multilayer assembly involving embedding nanoparticles and other functional layer constituents makes possible the fabrication of interactive nano-engineered systems (carriers) based on designed assembly of nanostructured materials and enable to remote controlled delivery of substances of chemical and biological importance and interrogation to the environment while these capsules are delivered. These systems are aimed to navigate, activate the release of biologically active molecules and to report about local environment based on optical, ultrasound, radiofrequency and magnetic addressing, signalling and imaging. Optical and magnetic addressing and interrogation of capsules

has been illustrated on cell culture level. Perspectives and anticipated obstacles of remote controlling microcapsules delivery and activation are under discussion.

COLL 509

Photoactivatable estradiol-tethered surfaces for the study of estrogen non-genomic signaling pathways

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In addition to its role in the regulation of sex-related processes through gene transcription, 17 β -estradiol (E2) also activates estrogen receptors on the plasma membranes to elicit non-nuclear signaling. Approaches have been developed to distinguish experimentally non-genomic pathways from genomic ones, but the mechanism of the interactions between E2 and estrogen receptors on the plasma membrane remains unclear. We designed photoactivable estradiol-tethered surfaces to monitor spatial and temporal aspects of the E2 non-genomic signaling. A micropatterned glass substrate with 2- μ m gold spots was prepared by photolithographic techniques. The gold regions were functionalized with E2 and a photocleavable poly(ethylene glycol) (PEG), whereas the glass area was functionalized with the cell-adhesive cRGD peptide via a PEG-silane. This surface design permits E2 to become accessible only after photocleavage of the bulky PEG chains. The feasibility of this photoactivation strategy was studied by X-ray photoelectron spectroscopy and surface plasmon resonance measurements, complemented with cellular studies.

COLL 510

Toward rapid detection of biological particles using multivariable resonant label-free biosensors

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Significant achievements in transducers for biosensing have resulted in demonstrations of single molecule and single particle detection limits. These advances were demonstrated in pristine buffer conditions, often without interferences. Further, with the reduction of concentrations of biological molecules and biological particles, their diffusive transport to micro- and nano-sensors can easily take long time scales of days and even months, signifying the arrival to the limits of practical measurements. In this study, we apply our earlier developed multivariable resonant sensors for detection of biological (e.g. virus) particles in bioprocess fluids. The operation principle of our developed multivariable resonant sensors is based on measurements of the resonance

impedance spectra of the resonator followed by the multivariate analysis of the resulting sensor response. One of the key aspects of our developed transducers is the ability to reject interferences from the samples that contain species besides our target analyte particles. The design principles of the transducers will be discussed that include (1) designs of the transducers to enhance the sensitivity toward the analyte particles and (2) designs of the sensing region to reduce the diffusion time of biological species to the transducer surface and thus, reduce the time requested for biological detection.

COLL 511

Activatable theranostic systems

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Contrast agents used today are usually nonspecific. They typically reflect physiological changes associated with various types of diseases. Given the recent developments in molecular targeted therapies radiology is clearly lacking any more specific agents, able to visualize biological processes specifically. Some agents closer to this goal are target agents, e.g. prototypical targeted agents in the form of monoclonal antibodies labeled with signal-producing labels for MRI, optical or nuclear imaging. However, targeted agents only provide information on the expression/translation of a given target but not on its biological activity. Activatable agents however provide unique information on the biological activity of their target (or the specific environment, e.g. pH) since they only become activated upon interaction with their designated target, resulting in a significant increase of the signal-to noise ratio. This process can at the same time utilized to specifically release therapeutic agents upon specific stimuli at the target location.

COLL 512

Switching and Sensing of Functional Polymers at Surfaces

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Nanoparticles can be attached to polymer brushes, and in this way offer the possibility of the sensing of environmental conditions in the vicinity of the interface. The interfacial properties can be monitored, and also switching and responsive surface behavior can be detected in-situ via optical signals. Surface Enhanced Raman Spectroscopy in addition allows for a local chemical sensing of species close to attached nanoparticles. While polymer brushes usually respond directly to the environment, a reverse response may be introduced by functional particles. Those particles for instance will swell in water and expose their increased hydrophobic surface. In this way a hydrophilic substrate can be switched to a more hydrophobic state when it is exposed to water. When the water is removed, the surface returns to the hydrophilic state.

COLL 513

Switchable biointerfaces for capture, culture and release of cells

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Cells are cultured on plastic or glass substrates and frequently require removal from the surface for downstream testing, for example using gene expression analysis. Having to terminate an experiment to analyze cells may be an expensive proposition when dealing with scarce primary cells or embryonic stem cells. We are interested in developing switchable surfaces for collecting small groups of cells from predefined locations. This presentation will describe electrochemically switchable hydrogel-on-ITO electrode surfaces that may be used for cultivation and on-demand retrieval of cells. We will also describe efforts to design photodegradable cell culture substrates that release cells upon UV exposure to predefined locations. Applications of these switchable biointerfaces for cell cultivation, cell harvesting and cell analysis will be highlighted.

COLL 514

Dual stabilized nanoengineered polymer capsules

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The layer-by-layer (LbL) technique has found widespread use for the nanoscale engineered assembly of materials, as it is simple, versatile and allows precise control over film properties such as thickness and morphology. Recently, there has been emphasis on the development of LbL capsules specifically engineered to respond to specific stimuli for therapeutic delivery applications or as microreactors.

The preparation of LbL polymer capsules stabilized by a combination of "click chemistry" and disulfide cross-linking is reported. The capsules obtained possess gateable permeability due to the reversible character of the latter cross-linking. Their pH responsive behavior as well as their permeability using a series of labeled dextrans was investigated in both the "closed state" (CuAAC and disulfide cross-linking intact) and the "open state" (CuAAC cross-linking intact). The potential of the capsules to reversibly encapsulate DNA was demonstrated.

COLL 515

Surprises and Open Questions with Janus and Multiblock Colloids

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This talk surveys emerging areas opened up by the directional interactions presented by the specially-designed spheres known as Janus. The “diblock” motif, mutually attractive on one domain and repulsive on another, makes this a prototypical system for elucidating, on a mechanistic level, how concepts of chemical reaction kinetics explain the development of stable and highly ordered nonequilibrium structures. With the “triblock” motif, spheres that attract one another on two polar regions but repel at the middle band, we go beyond this to demonstrate the self-assembly of a useful low-density lattice of spheres, the colloidal Kagome lattice, and visualize its aqueous assembly dynamics on the single-particle level. A newer area of opportunity is “dynamic self-assembly,” in which energy fed into the system as a control variable generates big surprises. The generalization of these design rules will be discussed.

*Work performed with Erik Luijten, Qian Chen, Jing Yan, Nobuhiro Yanai, Jie Zhang, Melinda Sindoro, Jonathan K. Whitmer, Sung Chul Bae, Moses Bloom, and Ming Han.

COLL 516

The Surface Science of Titania and Other Metal Oxides

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The surface science of metal oxides -- the investigation of their fundamental surface properties, and of the adsorption and reactions of molecules -- has experienced a dramatic growth during the past two decades. In this field titanium dioxide, TiO_2 , has evolved as the prototypical material. The surfaces of TiO_2 are well understood, can be prepared with a controlled density of intrinsic defects and hydroxyls, and have been used in a multitude of theoretical and experimental investigations. Results from such studies have led to insights that are relevant in a wide variety of applications, ranging from (photo-)catalysis to novel electronic devices.

In the talk I will present a personal perspective of TiO_2 surface science research, with emphasis on most recent results. I will show how we can monitor adsorption in a molecule-by-molecule fashion, and manipulate the motion of molecules and atoms across, into, and out of the surface. I will also briefly discuss other metal oxides, and point out opportunities and challenges that surface investigations hold in the future.

COLL 517

Shape control and symmetry breaking in the synthesis of colloidal nanocrystals

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Seed-mediated growth has emerged as one of the most effective routes to the synthesis of noble-metal nanocrystals with controlled sizes, shapes, and morphologies. The nanocrystals are, however, limited to a high level of symmetry as constrained by the inherent, face-centered cubic lattice of these metals. We recently demonstrated a facile and versatile approach (backed up by a clear mechanistic understanding) for breaking the symmetry of a cubic lattice and thus obtaining nanocrystals with highly unsymmetrical shapes. The key strategy is to induce and direct the growth of nanocrystal seeds into unsymmetrical modes by manipulating the reduction kinetics. It is clear that the diversity of possible shapes taken by noble-metal nanocrystals could be greatly expanded by incorporating a series of new shapes drastically deviated from the cubic lattice. This work represents another major contribution to the shape-controlled synthesis of metal nanocrystals.

COLL 518

Engineering pressure-sensitive nanoemulsions for enhancing ultrasound-mediated cancer therapy

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The use of acoustic cavitation (*i.e.* oscillating and collapsing microbubbles) in the treatment of cancer is hindered by the lack of reliable approaches to generate microbubbles directly within the solid tumor. To address this limitation, a pressure-sensitive perfluorocarbon nanoemulsion (PSNE) that can extravasate through leaky tumor vasculature has been engineered to serve as cavitation nuclei. Upon accumulation in tumor interstitium, the PSNE can be vaporized with focused ultrasound, resulting in a highly localized cavitation field. The cavitation field can be used to significantly enhance the absorption of ultrasound in solid tumors, thus reducing the time and acoustic power required for ablation. Additionally, the cavitation field can be used for localized delivery of therapeutics to malignant cells. The physical and material properties as well as the implications of this novel colloidal nanoparticle in cancer therapy will be discussed.

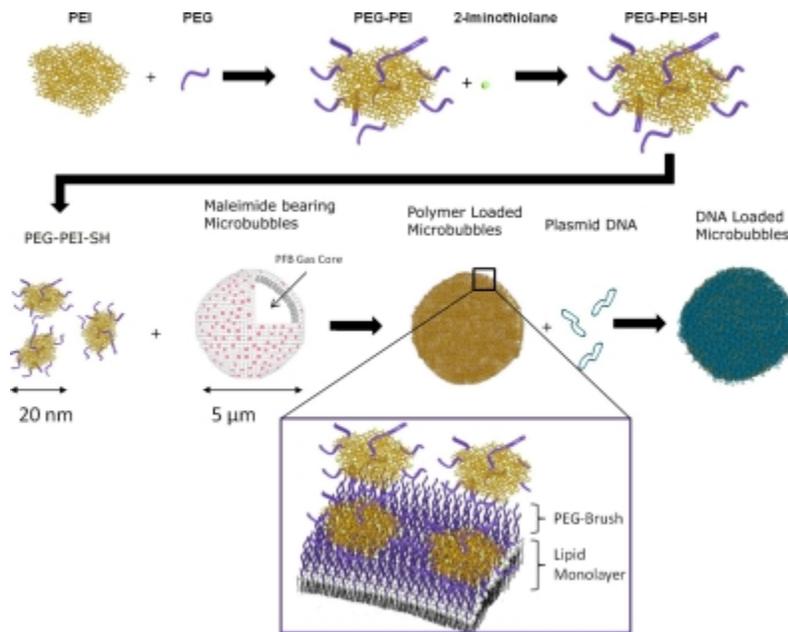
COLL 519

Polyplex-Microbubble hybrids for ultrasound-guided plasmid DNA delivery to solid tumors

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Microbubble ultrasound contrast agents are being developed as image-guided gene carriers for targeted delivery *in vivo*. In this study, novel polyethylenimine(PEI)-based polyplex-microbubbles were synthesized, characterized and evaluated for systemic circulation and tumor transfection. The PEI-microbubbles demonstrated increasingly positive surface charge and DNA loading capacity with increasing polymer content. Site-specific delivery to mouse xenograft tumors was achieved with targeted ultrasound following systemic injection of the DNA/PEI-microbubbles. Overall, polyplex-microbubbles offer control of DNA loading and packaging suitable for ultrasound-guided tissue transfection.



COLL 520

Controlled rupture of drug-encapsulated ultrasound contrast agent

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Monodisperse gas microbubbles, encapsulated with a shell of photopolymerizable diacetylene lipids and phospholipids, were produced by microfluidic flow focusing, as molecular imaging ultrasound contrast agents. The stability of the polymerized shell microbubbles in a bubble suspension and the acoustic stability under ultrasound insonation were significantly greater than for nonpolymerizable shell microbubbles and commercially available microbubbles (Vevo MicroMarker). The brightness intensity decreasing in the ultrasound images occurred at different powers of ultrasound depending on different polymerization times, indicating that the degree of polymerization controls the stability against acoustic rupturing. It was demonstrated that the polymerized shell microbubbles could be targeted by surface modification and bound specifically to cells through ligand-receptor interactions. Drug-encapsulated microbubbles were produced using a double-emulsion microfluidic focusing device.

COLL 521

Investigating the Acoustic Response of Gold Nanoparticle Coated Microbubbles

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Recent work has shown that solid nanoparticles can be used to control the stability of microbubbles used in ultrasound imaging and therapy and to provide other functional characteristics for example in multimodality imaging. The aim of this study was to investigate the influence of nanoparticle concentration and the preparation method used on the response of the microbubbles to ultrasound excitation.

Microbubbles coated with a surfactant and different concentrations of 15 nm gold nanoparticles were produced using either sonication, or a specially designed microfluidic device. The attenuation and backscattering coefficients from the bubble suspensions and the scattered response from individual bubbles were measured *in vitro* for a range of frequencies (1-7.5 MHz) and pressures (50-500 kPa). The gold nanoparticles were found to enhance the nonlinear character of the bubble response in agreement with previous theoretical work. The method of bubble generation was also found to significantly affect the acoustic response.

COLL 522

Imaging and retention of magnetic microbubbles at physiologically relevant shear rates

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Coated microbubbles, conventionally used as ultrasound contrast agents have shown great potential for therapeutic applications. To date however, targeting in vivo has shown limited efficacy. Magnetic microbubbles have been shown to increase gene transfection under combined exposure to ultrasound and a magnetic field in vitro and in small animal models. The aim of this work was to demonstrate retention of magnetic microbubbles under conditions relevant to human physiology. An ultrasound imaging phantom was designed and bubble retention tested for a range of flow rates, vessel diameters and magnetic field strengths and gradients.

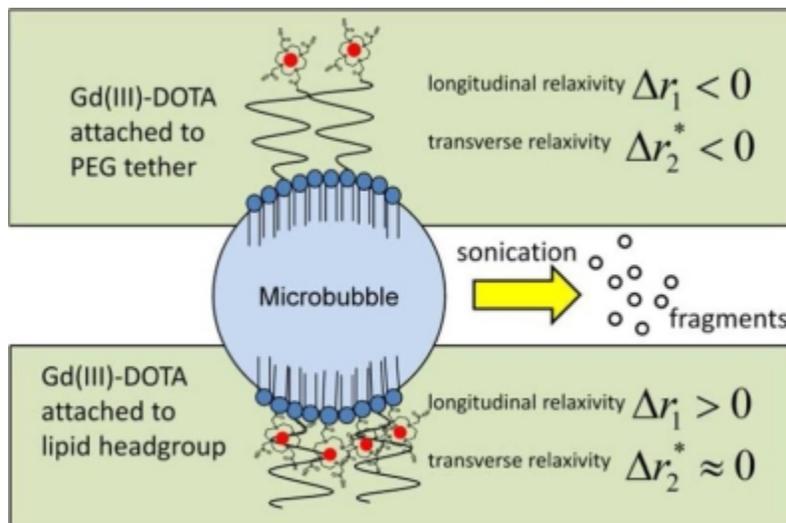
The results indicate that magnetic microbubbles can be retained using clinically feasible magnetic fields at shear rates ~1000/s and flow rates ~200 ml/min (corresponding to the capillary and arterial systems respectively). Preliminary results also indicate that a new formulation of magnetic microbubble generated using a new preparation technique shows higher retention efficiency than existing formulations.

COLL 523

Magnetic Resonance Properties of Gd(III)-Bound Lipid-Coated Microbubbles and their Cavitation Fragments

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NMR was used to compare the changes in relaxivity (r_1 and r_2^*) after fragmentation of microbubbles consisting of Gd(III) bound to two different locations on the lipid-shelled monolayer: the lipid-headgroup region and polyethylene-glycol brush. Our analysis revealed that fragmentation of the lipid-headgroup bound Gd(III)-microbubbles increased r_1 , but not r_2^* . In contrast, fragmentation of the polyethylene-glycol bound Gd(III)-microbubbles decreased both r_1 and r_2^* . Furthermore, the microbubble gas-core was revealed to enhance the transverse NMR signal but minimally affect the longitudinal signal.



COLL 524

Contents release from echogenic liposomes with dual triggers

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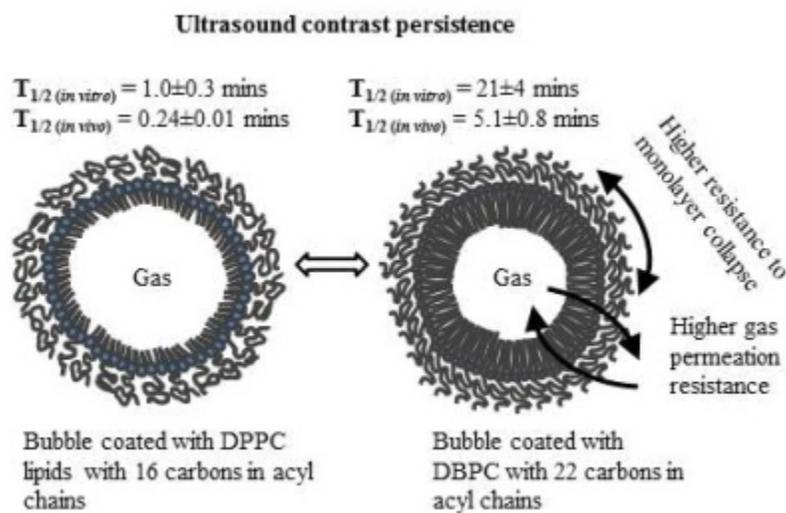
Liposomes are used extensively for targeting and delivery of anticancer drugs. However, this methodology frequently involves the passive release of the encapsulated drugs to the selected tissue sites. Matrix metalloproteinase-9 (MMP-9) is involved in the progression and metastasis of a large number of cancers. We demonstrate that MMP-9 mediated cleavage of substrate lipopeptides releases encapsulated contents from liposomes in the extracellular matrix of cancer cells. When the liposomes are echogenic, the release of the liposomal contents is further enhanced by the application of diagnostic frequency ultrasound. For release of liposomal contents in the cell cytosol, we have prepared polymer-coated, reduction sensitive, echogenic liposomes presenting the folate groups on the surface. These liposomes are actively targeted to cervical cancer cells overexpressing the folate receptor and efficiently internalized. The reducing environment of the cytosol rapidly releases the encapsulated anticancer drug from the liposomes, leading to cell death.

COLL 525

Enhanced circulation persistence of microbubbles coated with longer chain lipids

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Microbubbles are used extensively as theranostic agents for a wide range of biomedical applications. However, one limiting factor is their relatively short circulation persistence under physiological conditions owing to dissolution and clearance by the mononuclear phagocyte system. In this study, we varied the physiochemical properties of the microbubble shell by systematically increasing the acyl chain length of lipid constitutions and demonstrate that longer ultrasound contrast persistence of microbubbles can be achieved both *in vitro* and *in vivo*.



COLL 526

Soft micro-carriers for neuronal cell replacement therapies in the central nervous system

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Cell replacement therapy success in the central nervous system (CNS) depends equally on the transplanted cell type and on the cell delivery method. To improve neuron survival post-transplantation and long-term integration in the host brain, we have engineering soft cell carriers. Microgel particles were prepared using mono-dispersed emulsion droplets as polymerization reactors. The surface of the particles was treated for cell culture. After coating, the particles obtained promoted neuronal cell growth and permitted to release neurons at a later time without affecting neuronal processes. These

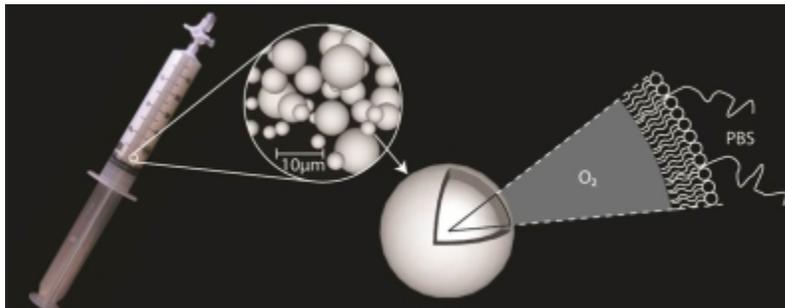
hydrogel particles facilitated neuron manipulation and enabled us to increase the number of viable transplanted cells in the young adult rat hippocampus while minimizing the amount of injected carriers. Taken together the properties of these microgel particles make them promising neuron micro-carrier to improve neuronal cell transplant, and could become the next generations of cell delivery supports.

COLL 527

Design of Lipid-Coated Microbubbles for Oxygen Delivery

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Injectable oxygen delivery is an emerging technology that presents an opportunity for improved patient care in a number of medical disciplines. Here, we report on the fabrication and characterization of novel encapsulated oxygen microbubbles (OMBs) designed for intravenous injection. The encapsulation is designed to mimic the alveolar lining (lung surfactant). The nano-thick encapsulation provided OMBs small enough for transcapillary passage: 99% of the microbubbles were less than 3- μm diameter, and less than 1% of the oxygen was encapsulated in microbubbles greater than 8- μm diameter. The OMBs were remarkably stable, losing less than 40% of the encapsulated gas over 12 days. Upon injection into an oxygen-depleted saline solution, the protein OMBs rapidly equilibrated by releasing their oxygen core. These results indicate that protein microbubbles may serve as a suitable platform for direct injection of bioactive and therapeutic gases.



COLL 528

Protein Analogous Micelles: Versatile, Modular Nanoparticles

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Peptides are functional modules of protein macromolecules that can be displayed apart from the whole protein to create biofunctional surfaces and interfaces, or can be re-

assembled in new ways to create synthetic mimics of protein structures. Each of these routes are being employed to gain new insight into protein folding and to develop new, functional, biomolecular materials. Examples of work from our laboratory in this area using peptide-lipid conjugate molecules (peptide amphiphiles) will be discussed relating to multi-functional surfaces, DNA-binding peptide assemblies, and protein analogous micelles for cancer and cardiovascular therapeutics.

COLL 529

Programming Micellar Nanoparticles with Biomolecules: Basic materials development and functional utility with respect to *in vivo* imaging

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The morphology of micellar nanoscale particles can strongly influence their physical and functional properties. Of great interest in our research is how nanoscale particle morphology may be utilized to influence, switch and optimize the *in vivo* properties of delivery vehicles for imaging and therapeutics applications. Therefore, we have set about developing a range of soft materials capable of switching morphology in response to specific biochemical stimuli. Herein, we present an approach that blends synthetic polymers with biopolymers to construct materials that respond selectively to particular enzymes including nucleases, proteases, transpeptidases, kinases and phosphatases. We will describe these polymeric micelles for their ability to selectively accumulate and target within tumor tissue *in vivo*.

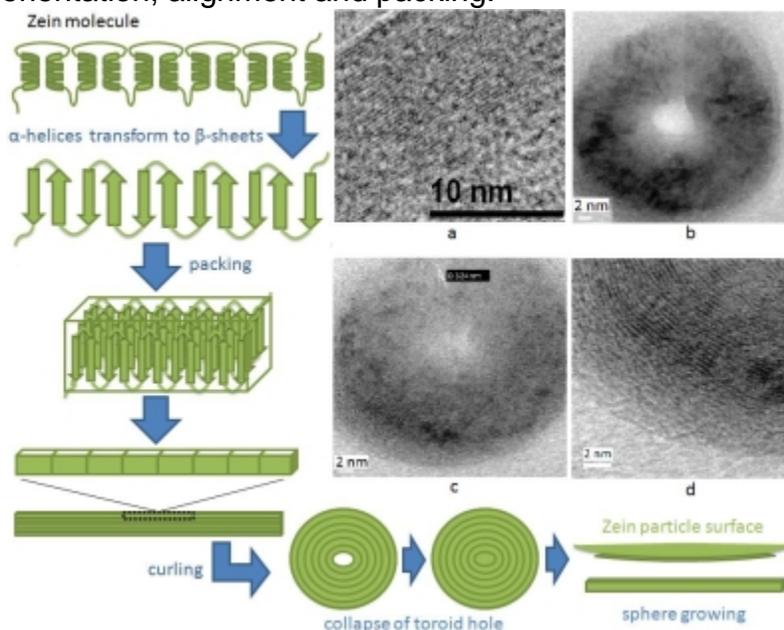
COLL 530

Nanoscale characterization of zein self-assembly

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Zein, a major protein of corn, is rich in α -helical structure. It has an amphiphilic character and is capable of self-assembly. Zein can self-assemble into various mesostructures that may find applications in food, agricultural, and biomedical engineering. Understanding the mechanism of zein self-assembly at the nanoscale is important for further development of zein structures. In this work, high-resolution transmission electron microscope (TEM) images revealed nanosize zein stripes, rings and discs containing a 0.35 nm periodicity which is characteristic of β -sheet. TEM images were interpreted in terms of the transformation of original α -helices into β -sheet conformation after evaporation induced self-assembly (EISA). The presence of β -sheet

was also detected by circular dichroism (CD) spectroscopy. Zein β -sheets self-assembled into stripes, which curled into rings. Rings formed discs and eventually spheres. The formation of zein nanostructures was believed to be the result of β -sheet orientation, alignment and packing.

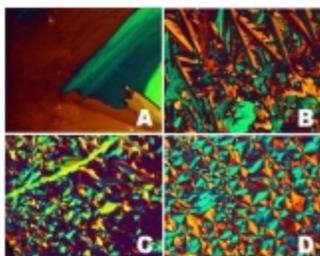


COLL 531

Characterization of the thermotropic and liquid crystalline properties of novel ion-pair amphiphiles (IPA)

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A series of IPA were synthesized from single- and double-chain quaternary- ammonium surfactants as the cationic counterpart and dodecylbenzenesulfonate as the anionic counterpart by ion-exchange metathesis reaction. Their thermal as well as liquid crystalline properties were studied with respect to the change in alkyl chain length of the cationic counterpart by Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Hot-Stage Polarized Light Microscopy (HSPLM). They show high thermal stability and exist as Smectic liquid crystals at room temperature.



COLL 532

Dynamic surfactants and networks: in control of soft matter properties by dynamic and dissipative self-assembly

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The self-assembly of small molecules, polymers, proteins, nanoparticles and colloids under equilibrium conditions has been a powerful approach for the construction of a wide variety of structures of nano- to micrometer dimensions. Nevertheless, the permanent nature of synthetic self-assembled structures does not compare well to the complex spatiotemporally confined self-assembly processes seen in natural systems, leading to e.g. dynamic compartmentalization of incompatible processes,

responsiveness, and self-healing. It remains a challenge to develop systems in which equilibrium and kinetics of self-assembly can be independently controlled.

In our research we focus on molecular approaches which allow independent control over interaction strength and dynamics: (i) the development of dynamic covalent surfactants and gelators, and (ii) dissipative self-assembly driven by a chemical fuel. I will discuss the background of our approaches together with recent results, and will suggest how dynamic self-assembling systems may lead to the next generation responsive, nanostructured or self-healing materials.

COLL 533

Toward rational design of protein-detergent complexes for in vitro membrane protein characterization

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The *in vitro* characterization of membrane proteins, and their interactions with other molecules, is critical to drug discovery. One of the largest roadblocks to these studies is the isolation of a protein of interest in its native conformational state within a membrane-mimetic environment. Micelles have traditionally served, and remain, as one of the primary systems for the formation of such so-called protein-detergent complexes (PDCs). Despite the vast number of surfactants that have been newly developed for PDCs, design rules for their selection and formulation to optimize protein stability and activity are lacking. This talk will provide a historical perspective on success in this area, and highlight some of our recent progress in developing rational design criteria for PDCs. Specifically, we report results of studies on PDCs containing non-ionic surfactants with added sterol derivatives, and their influence on the conformational stability of a human G-protein coupled receptor, hA₂aR. Combining detailed biophysical and microstructural studies on various PDCs reveals critical, quantitative parameters of micellar systems which can be used to optimize their formulation for a membrane protein of interest. Specifically, we find that optimal ligand binding activity of hA₂aR (a critical reporter of conformational stability) is strongly correlated with morphologies and sterol content which approximate those of the native mammalian cell membrane. This result, though seemingly intuitive, highlights the importance of aggregate structure over simple molecular chemistry in determining the success of micelle-based PDCs.

COLL 534

From Reverse Micelles to Reverse Vesicles: Principles for Modulating Self-Assembly in Nonpolar Organic Solvents

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It is well-known that self-assembly of lipids and surfactants in water leads to structures such as micelles and vesicles in dilute solution. In contrast, however, self-assembly in nonpolar organic solvents (oils) is much less studied. Standard textbooks in colloid science make only a brief mention of reverse micelles, which are typically assumed to be spherical. In the specialized literature, a few systems have been reported in which reverse spherical micelles can be transformed into reverse cylindrical micelles, typically upon addition of a polar substance like water. There is scant discussion of other non-micellar reverse phases such as reverse vesicles.

In our laboratory, we have found that reverse self-assembly is a much richer subject than is known, and it is full of interesting and surprising findings. For example, we have found that simple salts can influence the reverse self-assembly of lipids in oil (salts can be dissolved in oil only in the presence of lipid). Moreover, the nature of the salt cation is found to critically influence reverse self-assembly. For example, in mixtures with the unsaturated phospholipid, soybean lecithin we have found that salts of multivalent cations such as Ca^{2+} , Mg^{2+} , La^{3+} and Gd^{3+} induce the formation of reverse cylindrical filaments and in turn their organogels. This behavior is not seen with univalent cations like Na^+ or K^+ . Additionally, when combined with a saturated phospholipid, we have found that the same multivalent cations induce the formation of reverse multilamellar vesicles (reverse “onions”). Many of these results on reverse self-assembly can be rationalized based on molecular-geometry (packing parameter) principles, much like in the case of aqueous self-assembly.

COLL 535

Theory of micelle formation by protein-polymer conjugates

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Protein-polymer covalent conjugates are being developed for applications such as targeted drug delivery, protein therapeutics and enhanced cellular delivery of drugs crossing the blood-brain barrier. The conjugates may exist as single molecules or they can self-assemble to create multimolecular micelle structures. The polymer in the conjugate can be hydrophobic, hydrophilic or amphiphilic. The protein provides hydrophilicity depending on the charge and polarity characteristics. The self-assembly behavior is thus controlled by both the polymer and protein molecular properties. We develop a simple phenomenological treatment of protein-polymer conjugate micelles following the same approach we had developed previously to describe micelles formed of block copolymers. Additional interactions between the proteins due to their size and

charge effects are incorporated into the model. From the free energy minimization of the system, we calculate the critical concentration of the conjugates for micelle formation and the size of the micelles. We identify the essential physicochemical features of the polymer and the protein necessary for the conjugates to self-assemble into micelles. We compare the theoretical predictions against dynamic light scattering data obtained on Pluronic block copolymer - bovine serum albumin conjugates.

COLL 536

Characterizing the Different Mechanisms of Histone-Derived Antimicrobial Peptides

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Although the antimicrobial activity of full histones and histone fragments has been known for decades, relatively little research has investigated their mechanism of action. Buforin II, the best characterized histone-derived antimicrobial peptide (HDAP), is thought to target bacteria by translocating across the cell membrane and interacting with intracellular nucleic acids. Based on properties of buforin II and histone structures, my lab designed novel HDAPs. While one of our designed HDAPs shares a mechanism with buforin II, another appears to induce cell lysis. We have further emphasized the different mechanisms employed by HDAPs through a modular study of histone H2A derived peptides. This research has also considered the effects of combining "lytic" and "translocating" histone fragments into a single peptide. Together, these studies have started the systematic study of HDAP function, which will provide insights aiding in the design of future histone-derived therapeutic agents.

COLL 537

Structure and dynamics of "amyloid-like" lipid-protein fibers: FCS, FRET, FLIM and FRAP study

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Anionic membranes have been proposed to trigger "amyloid-like" fibril formation of several non-amyloidogenic proteins. In order to elucidate the key factors that govern the formation of these lipid-protein mixed assemblies (fibers), lysozyme was used as a model protein. The partition coefficients of Lysozyme-Alexa488 towards POPC:POPS LUVs were obtained from FCS. A cooperative partition model combined with the Gouy-Chapman theory described the variation of the mean fluorescence lifetime of Lysozyme-Alexa488 with the surface coverage of the liposomes, as well as homo-FRET

measurements, showing that Lysozyme-Alexa488 assembles into hexamers in the fibers. Advanced time-resolved FRET methodologies showed the formation of multi-stacked membranes at a low L/P ratio. FLIM measurements revealed that the fibers are homogeneous at the mesoscale level. Dynamic information was further obtained from FRAP data, revealing that both the phospholipid and protein diffusion is very slow in the fibers, indicating the formation of very rigid structures.

FCT (Portugal) is acknowledged for funding.

COLL 538

Using QCM-D to compare the actions of antimicrobial peptides alamethicin, chrysopsin-3, indolicidin, and SMAP-29 on a supported lipid membrane

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Antimicrobial peptides (AMPs) are produced by a variety of organisms as an essential component of their immune systems. Although AMPs are thought to kill bacteria through membrane disruption, the relationship between AMP structure and activity is not well understood. Quartz crystal microbalance with dissipation (QCM-D) was used to monitor the action of four AMPs: alamethicin, chrysopsin-3, indolicidin, and SMAP-29 (Sheep Myeloid Antimicrobial Peptide) on a supported phosphatidylcholine (PC) lipid bilayer. The four peptides representing diverse charge, hydrophobicity, and structural characteristics, interacted with the PC membrane distinctly differently as indicated by the QCM-D signatures of frequency and dissipation changes. Alamethicin, a practically neutral, α -helical peptide, inserted into the lipid bilayer beginning at AMP concentrations as low as 0.05 μ M. Chrysopsin-3, an α -helical peptide with 4 net charges, adsorbed to the membrane surface and formed pores below 5 μ M and lost lipid mass at 10 μ M, possibly due to the formation of peptide-lipid aggregates. Indolicidin, a short, tryptophan-rich peptide with random coil conformation, adsorbed to and inserted into the membrane, but no major membrane disruption was observed up to 10 μ M. SMAP-29, a strongly cationic peptide, adsorbed to the membrane and inserted to form pores, but did not cause significant loss of lipids from the bilayer. While the QCM-D signatures are very distinct between the four peptides, their unambiguous quantitative molecular interpretation requires additional, complementary methods of investigation.

COLL 539

Multiscale modeling of membrane insertion and self-assembly of helical peptides

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The precise mechanisms of spontaneous insertion and self-assembly of peptides in membrane remain poorly understood at molecular level. This limitation can be attributed both to the complexity of the problem and a lack of suitable molecular modeling tools for probing such complex processes. Conventional physics-based atomistic modeling could provide the ultimate level of details necessary for understanding the structure and dynamics of membrane proteins in pre-assembled forms, whereas so-called coarse-grained models are often necessary for interrogating the molecular process of how the system arrives at such functional states (i.e., insertion and self-assembly). We will present some of our recent studies in atomistic simulation of a series of M2GlyR-derived channel forming peptides as well as the development and application of coarse-grained models to understand the mechanism of membrane insertion and self-assembly.

COLL 540

Evaluation of a library of synthetic variants of the HIV fusion peptide in fusion, permeation and cell uptake assays

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We have synthesized a library of variants of the 23-residue fusion peptide domain found at the *N*-terminus of gp-41 glycoprotein of HIV. Our library was designed to address the biophysical importance of secondary structure, peptide flexibility, glycine content and location as well as the nature of the membrane anchor. Each member of this library also bears a positively charged hexapeptide at the *C*-terminus for solubility and to facilitate binding to negatively charged membranes. We assayed each peptide for its ability to induce lipid-mixing and lysis in synthetic vesicles. We further analyzed RNA cell uptake activity of the library. We find a wide range of cellular uptake yield of peptide-RNA complexes, even for peptides with identical amino acid composition; a majority of peptides are not active in knock-down, presumably due to trapping of siRNA in a peptide-complex.

COLL 541

Comparison of Reversible Self-Assembly of Amyloid Beta (1-40) and Amyloid Beta (1-42) Over Nano-Scale Gold Colloidal Surfaces

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A fiber formation of amyloid beta peptide (A β) is a hallmark of the Alzheimer's disease. We investigated a reversible self-assembly process of A β ₁₋₄₀ and A β ₁₋₄₂ over various sizes of gold nano-colloids ranging between 10 nm and 100nm in diameter. As solution was changed from basic to acidic condition, the color of the solution changed from red to blue. The pH value where this color takes place (pH_o) is regarded as the point where

the A β coated gold colloids possess no charge and indicating that an formation of intermediate of a fiber formation (precursor of fiber). As for A β_{1-40} coated gold colloids in water, there was a unique size dependence in pH_o. On the other hand, no significant size dependence was observed for both A β_{1-40} and A β_{1-42} coated gold colloid in dimethyl sulfoxide. We conclude that a particular interaction in water must be essential to conduct the reversible self-assembly.

COLL 542

Nanoscale surface characterization using instrumentation combining atomic force microscopy and infrared spectroscopy (AFM-IR)

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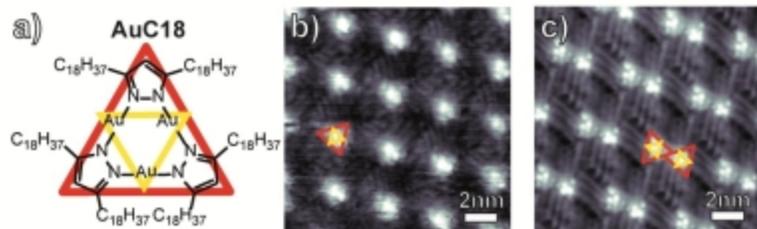
Atomic force microscopy (AFM) and infrared (IR) spectroscopy have been combined in a single instrument capable of producing 50 nm spatial resolution IR spectra and images. This new capability enables the spectroscopic characterization of surfaces and interfaces at levels not previously possible. A tunable IR laser source generating pulses on the order of 10 ns was used for excitation of cast sample films or thin cross sections deposited on IR transparent ZnSe prisms. Short duration thermal waves, due to infrared absorption, were studied by monitoring the resulting excitation of the contact resonance modes of the AFM cantilever. Differences in the IR spectra and contact resonance frequencies as a function of spatial position provide insight into the molecular structure and mechanical properties of surface features.

COLL 543

Scanning Tunneling Microscopy studies of trinuclear gold(I) pyrazolates

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Trinuclear gold(I) pyrazolates can bind strongly to electron-poor aromatic compounds, and are therefore promising for the use in selective sensors. STM was used to study layers of **AuC18** at the 1-octanoic acid/graphite interface, and different morphologies, monomeric and dimeric, were observed. Dynamic aspects of the layer were also studied on the molecular level, showing rotation of dimer pairs. Insights into such dynamics on the surface will be of great importance for the understanding (and control) of molecular monolayers.



COLL 544

Atomic-level Defects in ZnO: Is Characterization Possible?

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Inclusion of amphoteric zinc oxide (ZnO) thin films in energy conversion technologies such as photovoltaics and batteries requires advancement in nanometer-scale control over the morphology and chemical composition of the near-surface region; intrinsic and extrinsic doping of the layers to improve conductivity; and rates of interfacial charge transfer to enhance charge injection or extraction. The following extensive theoretical and experimental protocol is used to understand the role of interfacial defects on interfacial charge transfer all as a function of oxygen content in synthesis gas for sputtered ZnO samples: x-ray photoelectron spectroscopy to identify the presence of surface defects (hydroxyls, oxygen and zinc vacancies, zinc interstitials, and gallium dopants); DFT calculations, photoluminescence, and ultraviolet photoemission spectroscopy to evaluate the energetics of mid-gap states; extended x-ray absorption fine structure (EXAFS) measurements to determine interatomic distances. Connections are made with application-based electrochemical measurements and organic photovoltaic device performance.

COLL 545

Observations at the single-molecule level of the formation of nitrogen atoms on the Pt(111) surface from the reaction of ammonia with molecular oxygen

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Atomically resolved images of the interaction of ammonia with chemisorbed molecular oxygen on a Pt(111) surface have been obtained with a scanning tunneling microscope (STM) operated at 5 K in ultrahigh vacuum. Adsorption of NH₃ onto a structure formed by preadsorbed O₂ molecules results in a structure indicative of an NH₃-O₂ complex. Annealing of the ammonia-oxygen overlayer to 400 K produces a well ordered p(2×2) overlayer. For annealing temperatures slightly less than 400 K, the nitrogen is present in

a mixed $p(2 \times 2) + (\sqrt{3} \times \sqrt{3})R 30^\circ$ overlayer. Exposure of the N-covered surface to $H_2(g)$ reveals the formation of NH molecules, which can be distinguished from N atoms in several ways. Also apparent in the images are H atoms, which are highly mobile and easily moved by the STM tip. This work provides new insights into the formation and hydrogenation of nitrogen atoms on platinum surfaces.

COLL 546

Surface patterning of polypeptoids and investigation of thermo-responsive properties using scanning probe microscopy

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Nanoscale surface test platforms will be used to investigate phase transitions of copolymer nanostructures using scanning probe microscopy (SPM). Aqueous solutions of the random copolymer poly[(N-ethyl glycine)-*ran*-(N-butyl glycine)] P(NEG-*r*-NBG) become cloudy upon heating and clear upon cooling, which indicates reversible phase transitions. Changes in the composition of copolypeptoids can be used to adjust the cloud point temperature within the range of 20-60 C. Nanopores within a film of octadecyltrichlorosilane were prepared using particle lithography and solution immersion. A pre-synthesized copolymer such as P(NEG-*r*-NBG) can be anchored to the sites of nanopores. The morphology and surface arrangement of brush polymer nanostructures can be characterized with SPM. Studies of thermo-responsive properties can be accomplished using dynamic protocols and liquid imaging media. A temperature stage can be used to heat the sample during time-lapse SPM imaging. Significant advantages are gained by localizing and patterning polymer brushes on surfaces for studies of thermo-responsive properties.

COLL 547

Interfacial diffusional dynamics of dyes in ionic liquids near solid surfaces

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Room-temperature ionic liquids (RTILs) have been widely used in many energy related applications such as fuel cells, photovoltaics, supercapacitors, and batteries. However, some of the most fundamental questions about the interfacial dynamics of ionic liquids at solid electrode surfaces remain unanswered. We report interfacial diffusional dynamics of rhodamine6G in *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, $[C_nMPyr][Tf_2N]$, ionic liquids by controlling the gap of two solid surfaces within a tens of nanometers range on an inverted fluorescence microscope platform. The effect of variable gap nanoconfinement on the diffusional dynamics will be discussed.

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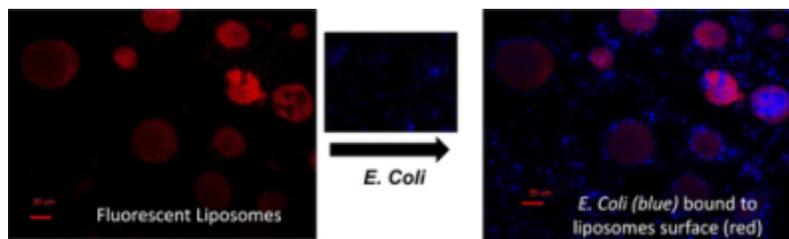
COLL 548

Design and optimization of optically responsive biosensors

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Liposomes are of great interest to the scientific community for their use to convey vaccines, drugs, enzymes or other substances to target cells or organs and sensing of various molecules. Conjugated polydiacetylene (PDA) liposomes have environmentally sensitive optical characteristics which make them excellent sensors for the detection of virus, proteins, DNA, toxins and biologically relevant molecules like glucose.

We describe here an approach for highly-sensitive protein sensors based on the changes in optical properties of the polydiacetylene (PDA) liposomes following chemical reactions at the liposome surface which amplified the optical signal. We present our preliminary results on the design and optimization of chemically modified PDA liposomes and their enhanced sensing towards various proteins. Various analytical techniques such as UV-Vis and fluorescence spectroscopy, Fluorescence microscopy, Fluorescence Anisotropy Fluorescence resonance energy transfer (FRET), Infrared spectroscopy and Mass spectrometry are being used to understand the biosensor device. We expect to attain sub-nanomolar or lower detection limits of various proteins through an amplification process. The objective of present study is to enhance the sensitivity of PDA liposomes and to better understand the interactions of protein molecules with bilayers of liposomes.



COLL 549

Adatom-Induced Self-Assembly of Aromatic Isocyanides on Au(111): Energetics, Structure and Work function

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The self-assembly of organic molecules on metal surfaces is of great interest for their central role in the development of molecular-based electronic and optical devices. In this work, we have investigated the adsorption of 1,4-phenylenediisocyanide (PDI) and 4,4'-biphenyldiisocyanide (BPDI) on the Au(111) surface through a combination of density functional theory (DFT), two-photon photoemission (2PPE) spectroscopy and low temperature scanning tunneling microscopy (STM). Our calculations have confirmed the adsorption structure and energetic stability of the adatom-induced, self-assembled molecular chains of -[PDI-Au]- and -[BPDI-Au]- motifs observed by STM. The corresponding adsorption energies were computed to be more than half eV larger than those of the vertical adsorption motifs in which only one isocyanide is bound to the gold substrate. It was found that substantial charge exchange occurs at the molecular-chain/substrate interface, and the magnitude of the induced surface dipole moment depends on both the coverage and the packing pattern of the one-dimensional molecular chains. The computed surface potential shift of -1.5 eV for the interlocked, closely-packed -[PDI-Au]- chains on Au(111) was in excellent agreement with the measured work function reduction from 2PPE measurements.

COLL 550

Reactivity of highly-hydroxylated TiO₂(110) surface prepared via carboxylic acid adsorption and photolysis: STM, TPD, PSD and DFT studies

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The formation and chemistry of a highly-hydroxylated TiO₂(110) surface was examined at the atomic level by a combination of scanning tunneling microscopy, temperature-programmed desorption, photo stimulated desorption, and density functional theory. TiO₂(110) surfaces with an OH_b coverages up to 0.5 ML were prepared via a novel, photochemical approach using trimethyl acetic acid (TMAA) dissociative adsorption and subsequent photolysis at 300 K. Deprotonation of TMAA molecules upon adsorption produces both surface bridging hydroxyls (OH_b) and bidentate trimethyl acetate (TMA) species with saturation coverage of near 0.5 ML. The TMA species can be selectively removed by ultra-violet light irradiation while OH_b survive photolysis. The OH_b species typically occupy second-nearest neighbor sites along the bridging oxygen row locally forming linear (2x1) structures of different lengths, although the surface is less ordered on a long scale. The annealing of the highly-hydroxylated surface leads to hydroxyl

recombination and H₂O desorption with ~100% yield, thus ruling out the diffusion of H into the bulk. In agreement with experimental data, theoretical results show that the recombinative H₂O desorption is preferred over both H bulk diffusion and H₂ desorption processes.

COLL 551

Probing the interface of charged surfactants in ionic liquids by XPS

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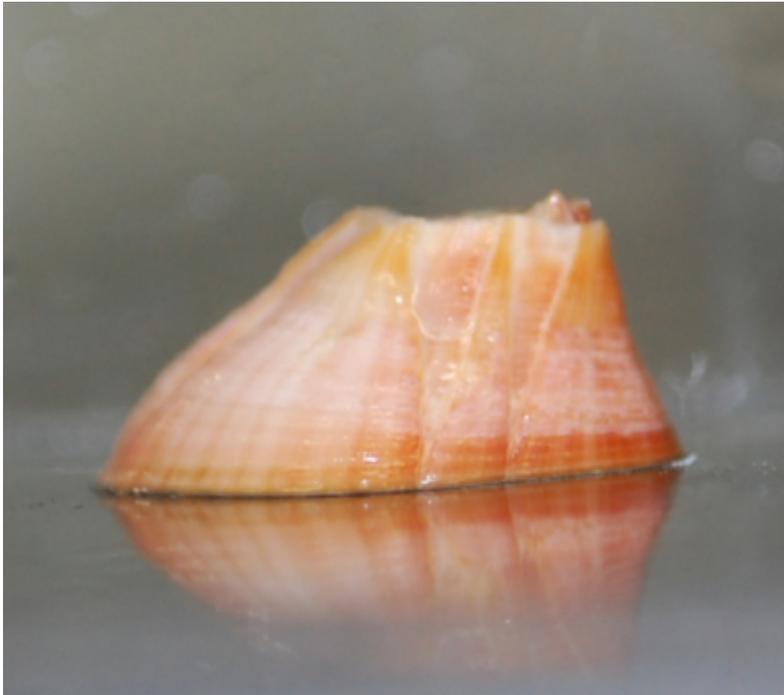
Room-temperature ionic liquids (ILs) are playing increasingly vital roles in many processes of both fundamental and applied natures such as separations and catalysis. It is therefore critical to obtain a better understanding of their interfacial properties such as surface charge and composition. Here we examine the influence of positively-charged surfactants on IL interfaces by X-ray photoelectron spectroscopy (XPS). The roles of surfactant alkyl chain length, concentration, and information depth on interfacial properties are investigated. Depending on the chain length and concentration, the surfactants can alter the IL interface to varying extents, highlighting a simple route to manipulate interfacial properties. XPS also reveals that surfactant counterions predominantly dissociate into the bulk. As a consequence, ion exchange occurs between surfactant and like-charged IL ion. Our results are a further demonstration of the ability of XPS to give insights into the surface activity and aggregation behavior in multi-component ionic liquid systems.

COLL 552

Barnacle underwater attachment: Molecular interaction to tightly attach two different materials in water

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Barnacles have been an intriguing target of research from both aspects of how to prevent their fouling and to learn about the natural manner of underwater attachment for bio-mimetic and bio-inspired research. Recent advances in the molecular dissection of barnacle cement have indicated the diversity of biological adhesives, and it is now evident that the molecular system for barnacle attachment is unique among the organisms so far studied. Molecular interaction to self-assemble and coupling to foreign surfaces will be discussed.



COLL 553

Bioadhesion the barnacle way

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Barnacles possess the ability to be either generalist or substrate-specific at the point of first attachment. Because of the complex metamorphosis in their lifecycle, the adhesive system used by adult barnacles is probably different from the larval adhesive produced at 'settlement'. The adult barnacle adhesive system fundamentally differs from other models such as tubeworm and mussel. Barnacle glands differ from other models in their general layout. As regards the proteins involved, otherwise ubiquitous amino acid residues are apparently missing in barnacle glue. A cross-linking mechanism to 'set' the protein complex has not been definitively shown. These observations mean that barnacles use novel methods to attain adhesion and to maintain cohesive strength on a variety of surfaces. These issues will be explored mainly in reference to *Lepas anatifera*, a notorious biofouler and generalist, attaching to diverse surfaces: wood, skin, glass and plastic.

COLL 554

Characterization and synthetic mimics of shellfish adhesives

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The oceans provide several compelling research topics within the contexts of understanding material-surface interfaces, biological adhesives, and design principles for biomimetic materials. We are particularly intrigued by the adhesives and cements used by several marine organisms for attaching themselves to substrates. Our laboratory is working to characterize the glues of shellfish such as mussels and oysters. Spectroscopy, biochemical analysis, and mechanical testing are all providing insights on how these animals stick. These findings are then bringing about inspiration for creating synthetic polymer mimics of bioadhesive proteins. Such biomimetic work is reducing complex biomolecules down to relatively simple copolymer systems. These studies are helping to determine the minimum components required for function. The resulting polymers are exhibiting the ability to adhere more strongly than commercial Super Glue and also bond well underwater.

COLL 555

Synthetic water-borne underwater adhesives inspired by marine sandcastle worms and their use in deep tissue fixation

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Sandcastle worms build intertidal, reef-like colonies by gluing together sand grains with an undersea bioadhesive. The macromolecular components of the adhesive include at least 4 polybasic proteins, a set of polyacidic phosphoproteins, and polyacidic sulfated polysaccharides. The adhesive also contains Mg^{2+} , Ca^{2+} , and transition metals. The components are packaged and stored in the adhesive gland as pairs of oppositely charged macromolecules electrostatically condensed in distinct secretory granules. During application, the granules are ruptured and the contents mixed by paddle-ended cilia. The adhesive sets, triggered by a pH change, into a solid/liquid foam within 30 s after secretion, then is covalently cured by a co-secreted catechol oxidase enzyme through crosslinking of catechol sidechains. The natural adhesive inspired the development of synthetic underwater adhesives based on associative phase separation of oppositely charged polyelectrolytes—complex coacervation. Progress in development of adhesive complex coacervates for tissue fixation will be reported.

COLL 556

Multi-scale characterization of barnacle adhesive interfaces

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Barnacles have long attracted the attention of antifouling- and bioadhesion-focused researchers, however, most activity has been dominated by investigations of adult barnacles and their adhesion mechanism. Adult barnacles are specialists in adhering tenaciously to all manner of immersed surfaces, making their adhesive proteins interesting models for synthetic 'bio-inspired' glues. They are also the obvious culmination of the colonization of anthropogenic surfaces in the marine environment (biofouling) and are therefore targeted by many contemporary antifouling products. An argument can be made, however, that the cyprid, or settlement-stage larva of barnacles, is equally important if not more so. The cyprid is supremely adapted for selecting and adhering to surfaces that are optimal for growth and survival to adulthood. The cyprid has two separate adhesion mechanisms, one temporary and one permanent, that are apparently different to the adult adhesion system. Cyprids explore surfaces prior to settlement using a pair of stilt-like antennules. The temporary adhesive bond produced during this exploration process is tenacious, rapidly reversible and mediated by a complex adhesion system involving the morphology of the attachment discs, a liquid proteinaceous secretion and specific attachment and detachment behaviors. Our research aims to elucidate this system using a diverse range of techniques from atomic force microscopy of the temporary adhesive, to high-speed photography of attachment behavior and 3D tracking/imaging surface plasmon resonance of attachment events. Once a cyprid has selected an appropriate settlement site, it attaches permanently. The permanent attachment mechanism is almost entirely unknown, however novel insights provided by confocal microscopy-based contact angle goniometry of the adhesive on model surfaces suggest that the permanent adhesion process is no less complex than that of temporary adhesion. Either of these stages would be logical points of intervention for novel, environmentally benign, antifouling strategies and improvement of our knowledge surrounding them is therefore paramount.

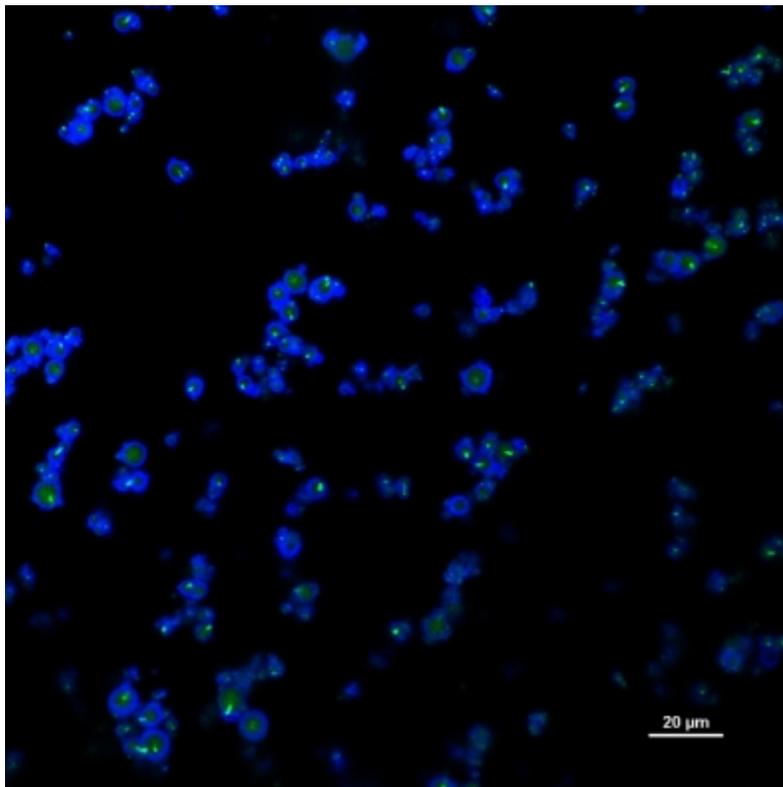
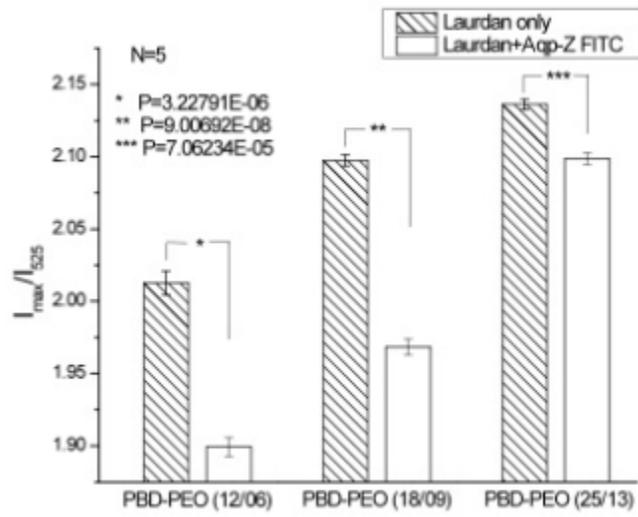
COLL 557

Mechanistic perspective on aquaporin-z incorporated block copolymer poly(butadiene-b-ethylene oxide) polymersomes

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The aim is to study the mechanistic effects of di-block copolymers in modulating the membrane tension and osmotic permeability of polymersomes. By systematically modulating the mechanistic effects of the diblock copolymer PBD-PEO in chain packing, diffusivity and rigidity of the polymeric chains, we can gain insights into water permeation mechanism through the block copolymer bilayer. The osmotic permeability through the polymeric bilayer would be retarded in accordance to bending rigidity

modulus the polymeric bilayer and hydrophobic thickness. The subsequent aim is to evaluate the effects of bilayer rigidity and hydrophobic/hydrophilic mismatch on channel protein activity, namely Aqp-Z, a novel transmembrane water channel protein



. When situated in different PBD-PEO bilayer, Aqp-Z exhibits distinctive activity profiles. This can be attributed by at least two global factors associated with the protein-polymer bilayer interaction: (1) hydrophobic/hydrophilic mismatch between Aqp-Z and its surrounding polymer bilayer; (2) dissimilar membrane tension in the surrounding polymer bilayer.

COLL 558

Effects of ethanol on liposome suspensions in water

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Effects of addition of ethanol in 150 nm average size large unilamellar liposome suspensions are studied primarily using dynamic light scattering. Average liposome size decreases as ethanol concentration increases till 20 vol%. Volume fraction of liposomes in suspension also decreases with ethanol addition but number density remains constant and scaled size distributions of liposomes for different concentrations of ethanol are self-similar. These two results together indicate that reduction in size upon addition of alcohol is not due to breakage and coalescence of vesicles but as a result of shrinkage of each liposome. Diluting liposome suspension containing 20 vol % of ethanol by addition of water causes liposomes to nearly regain their original size at that concentration; thus indicating the size change is reversible. Cryo - transmission electron microscopy and ^{31}P NMR spectra also confirm that liposome size reduces. Structural investigation of liposome-ethanol interaction was done by Fourier transform infrared spectroscopy.

COLL 559

Positively K^+ -responsive membranes with functional gates driven by host-guest molecular recognition

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A novel positively K^+ -responsive membrane with functional gates driven by host-guest molecular recognition is prepared by grafting poly(*N*-isopropylacrylamide-co-acryloylamidobenzo-15-crown-5) (poly(NIPAM-co-AAB₁₅C₅)) copolymer chains in the pores of porous nylon-6 membranes with a two-step method combining plasma-induced pore-filling grafting polymerization and chemical modification. Due to the cooperative interaction of host-guest complexation and phase transition of the poly(NIPAM-co-AAB₁₅C₅), the grafted gates in the membrane pores could spontaneously switch from “closed” state to “open” state by recognizing K^+ ions in the environment and *vice versa*; while other ions (e.g. Na^+ , Ca^{2+} or Mg^{2+}) can not trigger such an ion-responsive

switching function. The positively K^+ -responsive gating action of the membrane is rapid, reversible and reproducible. The proposed K^+ -responsive gating membrane provide a new mode of behavior for ion-recognizable “smart” or “intelligent” membrane actuators, which is highly attractive for controlled release, chemical/biomedical separations, tissue engineering, sensors, and so on.

COLL 560

Stochasticity in E.coli synthetic gene network in response to osmotic stress

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Random noise or stochasticity in gene networks contributes to phenotype formation. A focus of our research efforts is to discern the influence of mechanical and osmotic stress that build up in tumor microenvironments being causal in metastatic phenotype formation. Osmotic stress is due to differences in the activity of water between the cell interior and the microenvironment. We have investigated how the difference in water activity causes stochasticity in a synthetic gene network in *E.coli*. A synthetic gene network consisting of three genes in a cascade that are sequentially downregulated and reported by CFP and YFP, and fourth independent gene reported by RFP was subjected to osmotic stress NaCl and sucrose (0 – 3 M). The fluorescence intensities and self-correlation parameters for CFP, YFP, and RFP expression, and intrinsic, and extrinsic noise parameters for *cfp-yfp*, *cfp-rfp*, and *yfp-rfp* gene pairs determined from the respective protein expression exhibit a combined repression and activation depending on activity of water. Stochasticity in gene expression is almost entirely due to intrinsic noise which decreases in the order *cfp-yfp*>*yfp-rfp*>*cfp-rfp*. Differences between NaCl and sucrose as solutes were observed and could indicate the participation of mechanosensitive ion channels on the membrane wall. Significant results of these studies will be presented.

COLL 561

Tuning substrate viscoelasticity and patterning in polymer-tethered lipid bilayers

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Polymer-tethered lipid bilayers comprised of phospholipids and precisely controlled concentrations of physisorbed lipopolymers represent an exciting model membrane platform characterized by tunable viscoelastic properties. Lipopolymers have been shown to act as diffusion obstacles that manifest as changes in bilayer fluidity.

Additionally, experiments indicate that elevated lipopolymer densities result in biaxial stress leading to the formation of membrane buckling structures that can be linked to a membrane's elastic properties. Patterned model membrane architectures can be fabricated to exhibit stable lateral gradients in lipopolymer density or sharp boundaries between areas of high and low lipopolymer densities. Such patterns can be visualized and characterized on the basis of lipopolymer density-specific membrane buckling structures using epifluorescence and atomic force microscopy. The ability to precisely regulate mechanical attributes potentiates the use of these lipopolymer-lipid supramolecular assemblies for a range of applications, including cell substrates capable of exploring cellular mechano-sensing. Findings from such applications are discussed.

COLL 562

Role of membrane germinant receptors GerH and GerS of *Bacillus anthracis* on invasion of macrophages and cytokine response

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Ger receptors on the membrane of *Bacillus anthracis* are believed to be only responsible for germination of *B. anthracis* spores; however, the role of Ger-receptors on virulence and immune responses of macrophages is poorly understood. Macrophages were infected with wild-type *B. anthracis* 34F2, the *gerH*⁺ and *gerS*⁺ strains expressing only GerH or GerS receptors, and *ger*_{null} spores lacking all germinant receptors. Germination and growth of spores inside macrophages and their ability to elicit a cytokine response were investigated. *B. anthracis* 34F2 and *gerH*⁺ interacted strongly with macrophages by germinating and lysing phagocytes. *GerS*⁺ and *ger*_{null} mutants failed to germinate and lyse macrophages. However, all strains elicited a strong cytokine response suggesting that cytokine expression is due to either the release of toxins from vegetative *B. anthracis* or by macrophage-spore interactions. Our study suggests that Ger-receptors on *B. anthracis* may also be responsible for the cytokine response of macrophages after spore-cell interaction.

COLL 563

Synthesis of Metallic Nanoparticles on Semiconductor Thin Films

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Optically active metal nanoparticles have been of recent and broad interest because of their ability to enable high sensitivity enhancements in various optical detection techniques. Metal nanoparticle films directly attached at surfaces have the advantage of

significant optical enhancement arising from small interparticle gaps (e.g. stable hot spots) Here, we report synthesis of metallic nanoparticles (Ag or Au) on a semiconductor thin films (Ge or Sn) that have uniform and controllable particle size distribution. The metallic nanoparticles are obtained by a simple redox procedure on the semiconductor surface. Controlling nanoparticle surface coatings in situ for molecular studies for Surface Enhanced Raman Spectroscopy and Whispering Gallery Mode based photonic-plasmonic coupling at ultra-low concentrations (e.g. approaching to single molecule) will be reported.

COLL 564

Gold Nanorod-Enhanced Light Absorption and Photoelectrochemical Performance of α -Fe₂O₃ Thin-Film Electrodes for Renewable Energy Conversion and Electromagnetic Enhancement Mechanism

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We present surface plasmon enhanced light absorption and photoelectrochemical performance of α -Fe₂O₃ thin film electrode modified with well-defined gold nanorods (NRs). The photoelectrochemical reaction of the plasmon active substrate for water oxidation reaction is performed and compared at various hematite layer thicknesses. Pronounced absorption enhancement of α -Fe₂O₃ in the visible spectra corresponding to the surface plasmon of gold is observed. When the bias potential is increased to +0.5 V (vs. Ag/AgCl), a plasmon enhancement of the photoelectrochemical reaction of water oxidation at wavelengths near the plasmon resonance condition is observed for a thin α -Fe₂O₃ film accompanying a dramatic increase in the background double layer charging current. The significant increase in photocurrent in the region of surface plasmon absorption is attributed to the enhanced visible light absorption of the hematite thin film in the presence of the plasmon active gold nanorods.

COLL 565

Comparison of photo-degradation of 2,4-dinitrotoulene by silver doped and undoped titanium dioxide thin film in the presence of solar and uv light

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The photo-degradation of 2,4-dinitrotoluene (2,4-DNT) under illumination of solar light and uv in the presence of different amounts of photocatalysts (Ag-TiO₂ and TiO₂ thin films) and different Ag loadings was explored. In this study, silver doped TiO₂ (Ag-TiO₂) and undoped TiO₂ nanocrystalline films on glass substrates were prepared by a sol-gel method based on the self-assembly technique with nonionic surfactant to control the nanostructure. Microscopic and spectroscopic techniques were employed to characterize particle size, chemical composition, surface morphology, and the valence state of the Ag-TiO₂ film. The photocatalytic activity of Ag-TiO₂ thin films with different Ag loading and catalyst amounts for the degradation of 2,4-dinitrotoluene (2,4-DNT) under solar and uv light was evaluated. The degradation of 2,4-DNT followed first-order kinetics. There was negligible leaching of silver from the Ag-TiO₂ thin film though the leaching increased as the total Ag-TiO₂ photocatalyst increased. The degradation intermediate products of 2,4-DNT were analyzed by high-performance liquid chromatography and gas chromatography-mass spectrometry. Results on the role of silver loading on the morphology of the silver islands, degradation kinetics, and reaction intermediates will be discussed. Reaction pathways will also be presented.

COLL 566

Detailed mechanism for the polarization switching of nanorod plasmons

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We describe and demonstrate an electro-optic material capable of orthogonally switching the polarization of the localized surface plasmon resonance (LSPR) scattering of single gold nanorods, independent of their orientation. Liquid crystal (LC) samples were prepared in a sandwich configuration with electrodes theoretically capable of switching the LC 5CB from homogeneous nematic (HN) phase to twisted nematic (TN). We provide support for this proposed mechanism via Jones calculus by modelling the effect of ideally aligned HN- and TNLC on polarized light using similar physical parameters to experiment. The variable χ describes the phase retardation of light through the LC cell, and is defined as $\chi = (2\pi \Delta n d)/\lambda$, where Δn is the LC birefringence, d is the LC layer thickness, and λ is the LSPR wavelength. We find that the observed polarization as a function of the incident polarization can display a positive linear trend (when $\chi \sim 4\pi$ or other even values), a negative linear trend (when $\chi \sim 3\pi$ or other odd values), or a nonlinear trend (when $\chi \sim 3.5\pi$ or other half-integer values). Furthermore, the two linear trends provide the most reproducible orthogonal switching of LSPR polarization, and with a high degree of polarization for most output polarizations, with a large tolerance for inherent variations in LSPR wavelength and LC sample thickness.

COLL 567

Optical field enhancement of single silver nanoparticles studied with two-photon photoemission electron microscopy

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We use two-photon photoemission electron microscopy (2P-PEEM) to image the plasmonic response of spherical silver nanoparticles supported on a silver thin film. We determine electromagnetic field enhancement by measuring the photoelectron yield of the nanoparticles and the surrounding silver thin film. We find that the enhancement factors of the nanoparticles are, in some cases, 10^3 to 10^5 times greater than the photoemission of the bare silver film. We systematically investigate the dependence of the photoelectron yield as the diameter of the nanoparticle is varied. We present results for nanoparticle diameters of 20, 60, and 120 nm. The size-dependent enhancement factors are greatest for the larger particles. We also present a technique that determines the electromagnetic enhancement of the nanoparticle on a pixel-by-pixel basis. These enhancement factor images of single silver nanoparticles illuminated with femtosecond laser pulses (400 nm, ~ 3.1 eV) demonstrate that the greatest electromagnetic enhancement is localized at distinct regions on the surface of the nanoparticle rather than being uniformly distributed. Correlated scanning electron microscopy shows that local surface imperfections are responsible for the most intense regions of the PEEM enhancement factor images.

COLL 568

Probing Ground-State Single-Electron Self-Exchange Across a Molecule-Metal Interface

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We have probed single-molecule redox reaction dynamics of Hemin (Chloride) adsorbed on Ag nanoparticle surfaces by single-molecule surface-enhanced Raman spectroscopy (SMSERS) combined with spectroelectrochemistry. Redox reaction at the molecule/Ag interface is identified and probed by the prominent fluctuations of the Raman frequency of a specific vibrational mode ν_4 , which is a typical marker of the redox state of the Iron center in a Hemin molecule. Based on the autocorrelation and crosscorrelation analysis of the single-molecule Raman spectral trajectories and the control measurements of single-molecule spectroelectrochemistry and electrochemical STM, we suggest that single-molecule redox reaction dynamics at the Hemin/Ag interface is primarily driven by thermal fluctuations. The spontaneous fluctuation dynamics of the single-molecule redox reaction is measured under no external potential

across the molecule-metal interfaces, which provides a novel and unique approach to characterize the interfacial electron transfer at the molecule-metal interfaces. Our demonstrated approaches are powerful for obtaining molecular coupling and dynamics involving in interfacial electron transfer processes. The new information obtained is critical for a further understanding, design and manipulation of the charge transfer processes at the molecule-metal interface or metal-molecule-metal junctions, which are fundamental elements in single-molecule electronics, catalysis, and solar energy conversion.

COLL 569

Oxidation-resistant Ag nanostructures for ultrastable plasmonic applications

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From a fundamental materials perspective, Ag has the largest cross-section for visible light plasmonic interaction and amongst the highest surface enhanced Raman signal enhancement, even more so than Au. However, despite the fact that Ag is considered a noble metal, its surface oxidizes relatively quickly with exposure to ambient air. This degradation is deleterious to applications like surface enhanced Raman scattering (SERS) and surface plasmon resonance (SPR) sensing. Here we show that oxidation of Ag nanoparticles under ambient conditions can be significantly suppressed by contacting Ag with immiscible Co nanoparticles. We attribute this oxidation-resistance to a nanoscale galvanic coupling effect. Ag-Co bimetallic nanoparticle arrays prepared by pulsed laser dewetting self-organization have a sensitivity towards localized plasmon resonance sensing that is comparable to pure Ag but with significantly enhanced stability that ensures high sensitivity even after six months of storage in air.

COLL 570

Molecular Adsorption and Surface Charge Density of Colloidal Gold Nanoparticles Studied with Second Harmonic Generation

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Investigations on molecular adsorption and surface charge densities at colloidal gold nanoparticle interfaces are important for the development and optimization of applications such as plasmon-enhanced molecular sensing, catalysis, and photovoltaics. Second harmonic generation (SHG), using an ultrafast laser pulse at frequency ω to

generate light at 2ω , is a powerful technique for studying colloidal nanoparticle surfaces. The adsorption isotherm of the dye molecule, malachite green, adsorbing to gold nanoparticles in solution is measured using SHG to obtain the adsorbate site density and the free energy of adsorption. The surface charge density of colloidal gold nanoparticles is determined using SHG under varying salt concentrations. The results show excellent agreement with the modified Langmuir isotherm and the modified Gouy-Chapman models, and indicate that a Stern layer of adsorbed ions, image-charge attractions, and the nanoparticle surface curvature are all important considerations for a complete understanding of the colloidal gold nanoparticle surface.

COLL 571

Disk-on-pillar nanoarrays for sensing

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We present some of the more subtle aspects of how nanoparticles couple to light and each other, and how the nature of this coupling can affect the sensing properties of the system as a whole. As a first example, we investigate isolated disk-on-pillar structures, composed of a silicon pillar covered by thin layers of silica and silver, to understand the fundamental optical properties. Next, two-dimensional periodic arrays of these nano-elements are examined as a platform for surface-enhanced Raman spectroscopy (SERS) measurements. This system supports both localized surface plasmons and surface plasmon polaritons, whose interaction can be tuned to synergistically enhance the electric field resulting in larger SERS signals. Both of these examples highlight the importance of understanding the interplay between system components in plasmonic sensing applications.

COLL 572

Superomniphobic coatings made of magnetic nanostructures

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A robust method for the fabrication of arrays of magnetic nanowires by the combination of the porous membrane template method and colloidal lithography has been developed. The method allows for the regulation of density and dimensions of Ni overhang structures. These materials promise a number of micro- and nanofluidic applications involving the transport of microvolumes of liquids, suspensions, and particles; microfluidic agitation and mixing; alternation of wetting and adhesion using the remote control.

COLL 573

Polysaccharide-based responsive nanogels for controlled drug delivery

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The emerging importance of nanoparticles in drug delivery applications and the demanding needs of materials with biocompatibility and biodegradability have simulated efforts for engineering new materials based on new synthetic strategies. In the recent past, several advances have been made to synthesize hydrogels confined to micro- and nanometric dimensions (called micro- and nanogels).¹ Nanogels have properties similar to those of their macrogel counterparts with some additional benefits for drug delivery. In particular, their dimensions can ensure a rapid response to certain environmental stimuli, which is attractive for triggered drug delivery. The development of such systems from natural polysaccharides, which are biocompatible and biodegradable polymers, requires however well-defined chemical modifications to control the formation of hydrogels at the nanometer scale and their stimuli-responsiveness.

In this regard, we recently developed new approaches for the design of polysaccharide nanogels in physiological conditions. Using thiol-ene reactions and the aqueous core of liposomes as reaction vessels, we showed the ability to prepare well-defined chemical nanogels based on hyaluronic acid that can function as a template for multivalent conjugations for the triggered release of hydrophilic drugs.

Moreover, taking advantage of the ability of hyaluronic acid to specifically interact with cancer cells over-expressing the CD44 receptor, we developed HA-based nanocarriers for poorly water-soluble anti-cancer drugs using a simple, yet efficient, temperature-triggered self-assembly process.²

These new gel particles offer promising platforms for the controlled release of hydrophilic or hydrophobic drugs under certain external stimuli (magnetic field, light, irradiation, etc.).

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COLL 574

Hydrogel films consisting of temperature-responsive nanogels as an absorbent to capture CO₂ reversibly

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It has been reported that aqueous solutions of temperature-responsive nanogel particles consisting of poly(*N*-isopropylacrylamide-co-*N,N*-dimethylaminopropylmethylacrylamide) could capture and release CO₂ reversibly at a small temperature interval. Although, stoichiometric efficiency of the reversible CO₂ capture per amine in the solution was quite high, absolute amount of CO₂ per volume of absorbent was significantly lower than traditional amine absorbent, because concentration of nanogel in the solution was limited. Thus, nanogel solution requires high regeneration energy for the reversible use.

In this research, we report that pNIPAm based hydrogel films work as CO₂ absorbent. Our data shows that hydrogel films consisting of the temperature-responsive nanogel particles reversibly capture CO₂ with high stoichiometric efficiency. Effects of phase transition, water amount, crosslinker and amine content in hydrogel on CO₂ capture capacity were investigated.

COLL 575

Electrically Debonding Hydrogels of Polyvinylpyrrolidone

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The purpose of this work is to study debonding of polyvinylpyrrolidone hydrogels from aluminum surfaces under the effect of electric field. Adhesion strength of physical hydrogels to metals is relatively high. The normal load of 50 kPa is necessary to disconnect a sample of two aluminum surfaces joined by a 0.3-mm layer of a polyvinylpyrrolidone hydrogel. Application of electric field reduces the disconnecting load by at least ten times. Currents are observed due to ionization of water. Gaseous hydrogen is produced on the cathode interface. Power dissipation is observed in the sample.

This work was supported by funding received through Grand Challenges Explorations, an initiative created by the Bill & Melinda Gates Foundation.

COLL 576

Control and switching of protein adsorption and cell adhesion by polymer brushes made by the “grafting-to” approach

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Polymer brushes are a versatile tool to control and switch interfacial properties. By composing polymer brushes of two or more specific polymers/ polyelectrolytes a big variety of possibilities arises to control the interaction of those surfaces with proteins and cells. Using polymers responsive to environmental conditions as pH or temperature, the interfacial properties of mixed brushes can be switched. To use this possibility to switch protein adsorption too, it is essential to study swelling of complex brush systems as well as the mechanism and kinetics of protein adsorption in detail to identify the leverage for an adsorption/desorption control. This means to investigate protein adsorption on swelling brushes, and also the involvement of buffer components during dynamic adsorption processes. Based on this knowledge polymer brush systems were chosen to study their interaction with cells, with the aim to show the capability of polymer brushes to control cell adhesion and morphology.

COLL 577

Smart polymer brushes studied by in situ infrared ellipsometry

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Stimuli-responsive polymer brushes are of high interest for biotechnological and biomedical applications. Such brushes are functional surfaces for control of wettability, adhesion, friction, protein adsorption, and cell or bacteria growth. In this contribution infrared ellipsometric applications [1,2] for in-situ characterization are shown for various types of brushes (thicknesses of about 10-20 nm): pH dependent poly(acrylic acid) (PAA), mixed poly(acrylic acid)/poly(2-vinyl pyridine) (PAA/PVP), mixed poly(ethylene glycol)/poly(acrylic acid-b-styrene) (PEG/PAA-PS) brushes and thermoresponsive poly(N-isopropyl acrylamide) brush. The stimuli dependent changes of geometrical and chemical structure are discussed as well as the adsorption of proteins at such brushes which depends on surface and film properties. For example for PAA mono brushes the adsorption and desorption behavior for proteins can be tuned by variation of the pH value.

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COLL 578

Magnetic cellulose nanocrystals: demonstration and properties of organic-inorganic hybrid system

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We developed hybrid materials based on cellulose nanocrystals (CNC) to exploit their synergistic properties with magnetic domains. Inorganic nanoparticles were precipitated onto the CNCs using precursor salts that led to magnetic functions. In addition to particle characterization the magnetic properties of the materials were analyzed. We further demonstrate how these hybrid systems can be embedded into a polymer fiber mat to produce a magnetic nanocomposite and assess their applicability in magnetic separation processes. Together with other properties such as anisotropy, piezoelectricity and structuring, we demonstrate the ability for the developed hybrid systems to respond to magnetic fields which can open new applications for nanocellulose in the areas of responsive materials, optics and electronics.

COLL 579

Design, synthesis, and evaluation of novel triblock copolymers incorporating d-amino acid moieties

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Targeted drug delivery utilizing nanoparticle-forming polymeric systems is at the forefront of chemistry, biology and materials science. We are investigating a range of functionalized triblock copolymers composed of PEG and oligopeptide modules with the goal of elucidating superior candidates for encapsulation studies with clinically relevant anticancer drugs.

In this paper, we describe the design and synthesis of novel, tunable mPEG-oligopeptide triblock polymers (**MePEGNH-*b*-Poly-(crosslinking AA₁)_x-*b*-Poly-([*d*-AA₂]_y-co-[*l*-AA₃]_z)-NHAc**) that incorporate *d*-amino acid moieties in the hydrophobic core block. The impact of the *d*-amino acid moiety on physical properties (e.g. CMC, solubility, conformation) and formulation utility will be compared to more traditional triblock polymers that incorporate all *l*-amino acid residues.

COLL 580

Fabrication of bio-nanofibers into ordered architectures via external magnetic field

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Filamentous biomacromolecules, such as bacteriophage phage and flagella, are ideal bionanoparticles for the applications in nanotechnology, nanomedicine, and tissue engineering. However, how to control their assembly and surface patterning is still a challenge. In this study, we employed cationic magnetic nanoparticles (Fe_3O_4) to interact with ionic bionanoparticles (bacteriophage phage and flagella) and help them to assemble and align into ordered assembly with the aid of remote control of magnetic fields. We found that cationic magnetic nanoparticles and ionic bionanoparticles were associated with each other to form complex nanoparticles, where became ordered under the control of applied magnetic field (direction and strength). Such simple, effect strategy for bionanoparticles alignment over large areas remotely controlled by the external magnetic field is universal and can be applied to align different types of bionanoparticles into 2D fibrous arrays and 3D complicated structures on the substrates.

COLL 581

Thermoresponsive Nanostructures as “Smart” Draw Solutes in Forward Osmosis

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Forward Osmosis (FO) technology has been intensively studied for seawater desalination and wastewater treatment. It utilizes the osmotic pressure difference of two solutions separated by a semi-permeable membrane to induce spontaneous movement of water molecules from the less concentrated solution (feed solution) to the other solution (draw solution) while most solutes are rejected by the FO membrane. The selection of a suitable draw solute can greatly influence the efficiency of FO. Magnetic nanoparticles functionalized with hydrophilic molecules may generate high osmotic pressures. Although draw solute based on magnetic nanoparticles can be regenerated using magnetic fields, high field strength is generally required. Therefore, we designed a new class of “smart” draw solute -- thermoresponsive polymer-functionalized magnetic nanoparticles. With the assistance of thermal stimuli-induced aggregation, the nanoparticle draw solute can be readily recovered. In this presentation, our recent efforts on the fabrication of stimuli-responsive FO draw solutes will be discussed.

COLL 582

Can LUV with submicron size be a good model for bio-membrane?

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LUV (Large, Unilamellar Vesicles) is composed of self-assembled phospholipids as an enclosed bi-layer with diameter ranging c.a. 100 nm or larger. LUV is often used as a model to investigate structures and functions of bio-membrane and further as a vehicle for drug delivery. On the contrary, sizes of cells in nature are usually larger than 10 micron, and GUV (Giant Unilamellar Vecilces) is often used as a model. The objective of this study is to compare the physico-chemical properties of LUV and GUV to investigate the relevance of LUV utilization as a model of bio-membrane. We have found the translocation of Cell-Penetrating Peptides (CPP) into cytosol decreased when vesicle become smaller. The result indicates the contribution of lower mobility of lipid molecule at small vesicle causing CPP facing resistance to penetrate. Physiological meaning of such vesicle size will be further discussed at the presentation.

COLL 583

Diocetadecyldimethylammonium bromide/chloride: Monoolein liposomes for nucleic acid delivery

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One of the most prominent methods for therapeutic gene delivery is lipofection using cationic liposomes for the complexation, transport and release of nucleic acids into cells. Lipofection vectors are safe to consider for medical purposes as little mutational or toxicological risk exist.

Diocetadecyldimethylammonium Bromide/Chloride (DODAB/C): Monoolein (MO) liposomes have recently been reported to successfully promote animal cell transfection. The presence of MO, which serves as helper lipid in lipoplex formulations, influences the physicochemical properties of DODAB/C:MO liposomes and derived lipoplexes. Furthermore, lipoplex characteristics affect the interaction with extracellular components, uptake by cells and intracellular trafficking. The high biocompatibility of pDNA:DODAB/C:MO lipoplexes further supports this as a new gene therapy vector, using MO as new *helper* lipid in lipofection.

COLL 584

Nanobiopolymers: Efficient antimicrobials with membrane disturbant capacity

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Nanoparticles possess unique physicochemical properties, important for the efficient transport through the cell membranes. The small and controllable size, large surface area to mass ratio, and high reactivity facilitate the intracellular delivery, thereby overcoming some of the limitations in traditional antimicrobial therapeutics. Chemically modified biopolymers (thiolated chitosan and aminocellulose) were processed into nanoparticles via a one-step sonochemical process and evaluated for their antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. Thiolated chitosan and aminocellulose were shown to possess improved antimicrobial properties compared to the starting biopolymers and even higher bactericidal effect was observed after processed into nanoparticles. The mechanistic insights were obtained by Langmuir monolayer technique using *Escherichia coli* phospholipids as membrane models. The high cationic character of the modified biopolymers and the obtained spherical structure were found to allow efficient interaction with the phospholipid heads and tails, crucial for their antibacterial activity and transport through cell membranes.

COLL 585

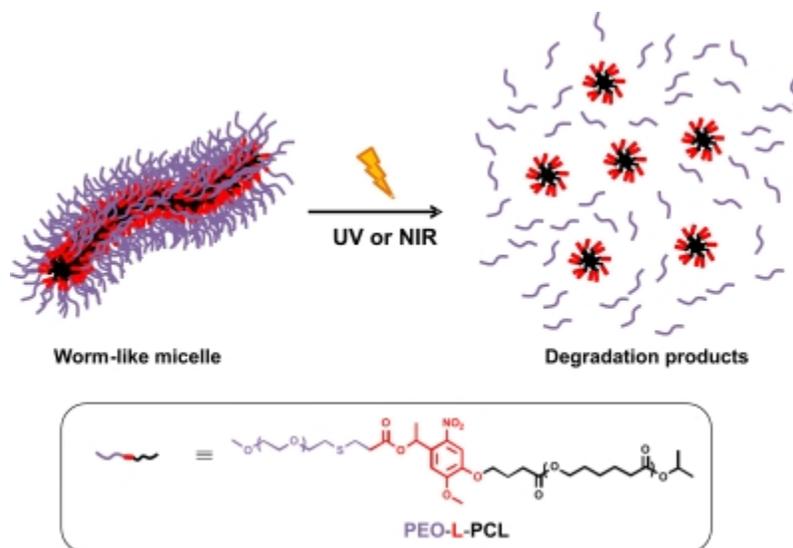
Photodegradable worm-like micelles for controlled drug delivery

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Worm-like micelles from degradable amphiphilic block copolymers are particularly appealing for drug delivery due to both their increased drug loading capacity and longer in vivo circulation times compared to their spherical counterparts.^[1, 2] The release of encapsulated hydrophobic drugs from these assemblies takes place by slow diffusion from the degrading micelles. Controlled release from the assemblies can be in principle achieved by the incorporation of stimuli-degradable linkers in the block copolymer. Here, we describe the synthesis, assembly and application of a block copolymer containing a photolabile linker between the polymeric blocks, poly(ethylene oxide)-L-poly(ϵ -caprolactone) (L = photolabile linker) which allows for a spatially and temporally controlled degradation. This block copolymer self-assembles into worm-like micelles and degrades under UV irradiation at 365 nm. Degradation experiments with near infrared irradiation will reveal its broader application in the biomedical field.

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COLL 586

Enhancement of cationic lipid - DNA complex properties by gemini surfactants and its impact in gene delivery

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Cationic lipid-mediated gene delivery constitutes a promising alternative to viral vectors. Cationic liposomes interact electrostatically with negatively charged DNA forming lipoplexes in which the nucleic acid is compacted and protected from the action of nucleases. Controlling the structure of lipoplexes is a critical task, since it determines the pharmacokinetics and transfection activity of these gene delivery systems.

We investigated the effect of condensing plasmids with cationic liposomes containing pyridinium cationic lipids developed by our group, in the absence or in the presence of increased amounts of pyridinium gemini surfactant. We determined the impact of co-lipid, its nature and amount used, presence of gemini surfactant and amount used, and cationic amphiphile/DNA charge ratio on formation and physicochemical properties of corresponding lipoplexes. We will present the interplay of these factors, in a comparative study, revealing the advantages conferred by gemini surfactants towards formulation and control of lipoplex size, physicochemical and transfection properties.

COLL 587

Multivalent Ionic Interactions in Multicomponent Polyelectrolyte Mixtures: From New Physics to New Materials

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Highly charged polymer chains in monovalent salt media exhibit a fairly simple range of behaviors, swelling in low salt, shrinking in high salt, based on the screening of repulsive electrostatic interactions among the segments. In the presence of other multivalent constituents, attractive forces arise. These attractions produce strong collapse of polyelectrolyte chains, adhesion between polyelectrolyte bearing surfaces, precipitation, and in the case of mixtures of oppositely charged polyelectrolytes, formation of fluid complex coacervate phases. We have measured the attractive forces between layers of polyelectrolyte brushes immersed in multivalent ionic media as a function of ionic strength. We have characterized coacervate formation in mixtures of model polyelectrolytes. We demonstrate how coacervate formation can be used to create new self-assembled materials, such as physically crosslinked hydrogels.

COLL 588

Responsive peptide-based triblock and star copolymers for delivery of therapeutics

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The self-assembly of amphiphilic block copolymers is dictated primarily by the balance between the hydrophobic core volume and the hydrophilic corona. In these studies, amphiphilic diblock, triblock and star copolymers containing poly(lysine) (PK) and poly(glutamic acid) (PE) were synthesized and their solution properties studied using dynamic light scattering, circular dichroism spectroscopy and transmission electron microscopy. These materials are shown to respond to pH, due in part to the helix-coil transition in the peptide chain, but also due to changes in curvature of the assembly at the interface. We exploit the responsiveness of these materials to encapsulate and release therapeutics such as doxorubicin and demonstrate the potential to achieve triggered release as a function of pH due to morphology transitions.

COLL 589

Star-polymers as Unimolecular Nanocontainers for Nucleic Acid Complexation

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The majority of nucleic acid–polymer complexes are formulated via self-assembly, a process that is often difficult to control and thus the desired nanoparticle properties are difficult to achieve. To address this issue we have synthesized a series of star polymers that act as unimolecular nanocontainers. We are able to precisely control the number of

short nucleic acids (siRNA, dsDNA) that are complexed by a star polymer and obtain even single nucleic acid–single polymer molecule complexes. These well defined star polymers are comprised of a cationic core and a neutral brush-PEG corona that insures colloidal stability. The nucleic acid–polymer complexes are well defined spherical particles with a narrow distribution (TEM, DLS) and are stable in PBS solution for days. Synthesis, thorough characterization and the study of the complexation process by isothermal titration calorimetry (ITC), Forster resonance energy transfer (FRET) and fluorescence correlation spectroscopy (FCS) will be presented.

COLL 590

On the pH Responsive, Charge Selective, Polymer Brush-Mediated Transport Probed by Traditional and Scanning Fluorescence Correlation Spectroscopy

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The complete and reversible charge-selective sequestration of fluorophores by a weak polyelectrolyte brush, poly(2-(dimethylamino) ethyl-methacrylate) (PDMAEMA) was examined using Fluorescence Correlation Spectroscopy (FCS). The chemistry and thickness of the weak polyelectrolyte PDMAEMA can be tuned reversibly between neutral and cationic polymer forms. Thus, by switching the pH successively, the brush architecture was tuned to selectively trap and release anionic dye probes, while continuously excluding cationic molecules. In addition, line-scan FCS was implemented and applied for the first time to a synthetic polymer system, and used to identify a new, slower diffusion time on the order of seconds for the sequestered anionic probe under acidic conditions. These results, which quantify the selective sequestration properties of the PDMAEMA brush, are important because they enable a better understanding of transport in polymers, and establish a spectroscopic means of evaluating materials with proposed applications in separations science, charge storage/release and environmental remediation.

COLL 591

Nanostructured multilayer coatings with antibiofilm activity for biomedical applications

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The formation of antibiotic-resistant biofilms on medical indwelling devices poses a critical problem for medical care. Controlling the adhesion and proliferation of bacteria on these surfaces is necessary to design antimicrobial and antibiofilm materials.

Acylase and α -amylase are proposed as efficient biofilm inhibitors, according to their ability to degrade the gram-negative bacterial quorum sensing signals and the exopolysaccharide matrix formed by biofilms, respectively. Nanostructured coatings built on medical devices surfaces prone to colonization (i.e. silicone) were produced using layer-by-layer (LbL) assembly technique. By alternate deposition of negatively charged enzymes and positively charged polyethylenimine a 10 bilayer film was assembled on silicone surface, as proven by Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) techniques. The nanostructured surface was found to be stable and bioactive, with improved wettability and antibiofilm properties, suggesting that it can be further applied in medical devices to counteract biofilm formation.

COLL 592

Old & new strategies in mass spectrometric imaging of biomaterials

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Matrix assisted laser desorption ionization (MALDI) mass spectrometry imaging is well established for the analysis of biomaterials and mammalian tissue, but suffers from various shortcomings including a difficulty in quantification and selective detection. Laser desorption vacuum ultraviolet postionization (LDPI-MS) is under development as an alternate to MALDI-MS for a variety of surface analysis and biological imaging applications including the analysis of antimicrobial surface coatings, bacterial biofilms, and animal tissue. LDPI-MS imaging quantification is demonstrated within the context of a polyelectrolyte multilayer that slow releases an antibiotic to inhibit early stage biofilm growth. While LDPI-MS has utilized nanosecond laser desorption, experiments suggest the potential of femtosecond laser desorption for depth profiling. Therefore, a new LDPI-MS instrument is described that permits three dimensional MS imaging at elevated pressure using femtosecond laser desorption combined with VUV postionization.

COLL 593

High Throughput Materials Discovery Adventures with Polymer Microarrays

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Polymer micro arrays have proven to be useful tools for the discovery of new synthetic materials to guide cell response to man made materials. This high throughput materials discovery approach is attractive because, the paucity of understanding of the cell-material interface hinders the *ab initio* rational design of new materials. The large number of polymer chemistries that can be investigated on a single polymer micro array act as a wide net in the search for materials that can achieve a certain cell response. A critical component of the materials discovery process is high throughput surface

characterisation employing chemometrics to handle the large amounts of complex data. Using this approach we have identified materials which show promise as substrates for pluripotent stem cell culture and coatings which resist bacterial attachment and biofilm formation with application in the reduction of medical device centred infection (Hook et al. Nature Biotech 2012).

COLL 594

Combing multiple surface analysis techniques to determining protein orientation on surfaces

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We use well-defined model systems and an array of surface analysis technics to study the protein orientation for the adsorbed protein fragments of Fibronectin (FnIII 7-10) on three different self-assembled monolayer (C₁₁, COOH, NH₂ and CH₃ terminated SAM's). By combing multi surface analysis techniques and statistical analysis we are able to determine the protein orientation. X-ray photoelectron spectroscopy (XPS) is used to quantify the amount of protein adsorbed on the surface and time of flight secondary ion mass spectrometry (ToF-SIMS) to characterize the orientation and conformation of the fragment. Spectroscopy methods are also included for more detailed information about bond orientation and the effect of dehydration. ToF-SIMS is very surface sensitive, sampling mainly the top portion of the adsorbed protein. Differences in amino acid composition for the ToF-SIMS analysis for the same protein on different surface can therefore be related to different orientation of that protein on the surface.

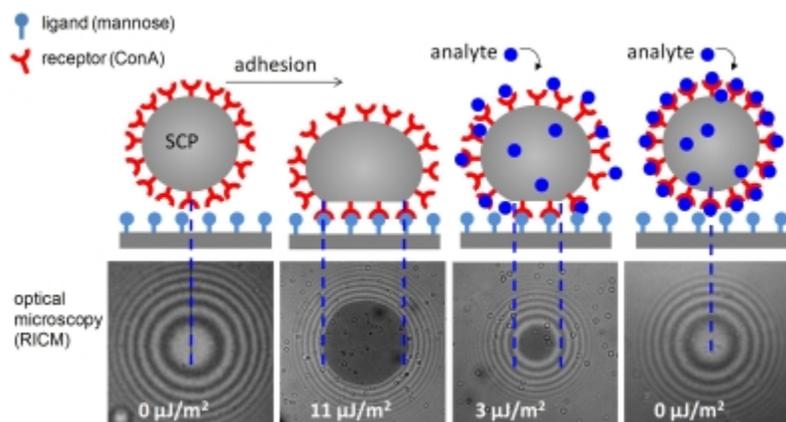
COLL 595

New force-based biosensors: mechanical deformations of soft colloidal hydrogel particles to quantify ligand/receptor interactions

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Many biological processes are mediated by ligand-receptor interactions of carbohydrates and proteins at interfaces. Although sufficiently sensitive to detect the majority of ligand-receptor interactions, standard methods like AFM or SPR pose limitations in sensitivity, robustness and handling. We introduce soft, deformable colloidal probes (SCPs) exhibiting mechanical deformations upon adhesion at ligand or

receptor interfaces as new sensing principle (Figure 1). This technique has a number of benefits: 1) high sensitivity and selectivity 2) inexpensive and easy to use 3) direct insights into colligative binding at biological/bioinspired interfaces.



As proof of the concept we studied the weak interactions between carbohydrates and lectins. The results yield direct insight into binding energies, cooperative binding events due to multivalent ligand presentation and indicated enhanced cooperativity as the elastic modulus of the hydrogel is decreased. Further, the method allowed to perform inhibition affinity assays by addition of various carbohydrate analytes including novel neoglycopolymers (Figure 1).

COLL 596

Nanofluidic cell for high-resolution, in-liquid transmission electron microscopy

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The capability to routinely perform high resolution transmission electron microscopy on samples in their native liquid environments would be a powerful addition to the biomedical and materials sciences fields, among others. We present transmission electron micrographs from nanoparticle samples imaged through ultrathin ($\sim 100\text{nm}$) layers of water. The image resolution and contrast degrade appreciably with increasing liquid layer thickness, making control over this parameter vital for achieving high resolution. We present a custom nanofluidic cell to deliver a number of unique performance features for high resolution electron microscopy. Ultrathin silicon nitride windows provide electron transparency while a carefully engineered flow path delivers the necessary control over the liquid thickness, along with the ability to reliably flow

liquid through the cell. We will demonstrate the capabilities of the cell using images of a variety of nanoparticle sizes and compositions, taken using different electron energies, in addition to different liquid layer thickness.

COLL 597

Micro-structural characterization of fibrous collagen hydrogels by two-photon fluorescence (TPF) and second harmonic generation (SHG) imaging

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Microstructure of hydrogels is an important design criterion in tissue engineering. Our understanding of the effects of physicochemical parameters and cross-linking reagents on the modifications of collagen microstructures within 3D hydrogels will be summarized. The micro-structures were detected non-destructively with two-photon fluorescence (TPF) and second harmonic generation (SHG) imaging. SHG images revealed the extent of modifying original microstructures within hydrogels and TPF outlined novel optical contrasts. SHG images of 37 °C assembled hydrogels helped to identify glyceraldehyde-induced remodeling of the original 5-10 µm long "fiberlike" collagen structures to 20 µm and longer aggregated strands. Different behavior took place upon cross-linking 27 °C assembled hydrogels with the same chemical. The cross-linking and induction of fluorescence took place along and in-between SHG generating 60 µm fibrillar clusters. Some newly-formed fluorescent features had no corresponding SHG signals in the equivalent optical plane. Findings will be discussed with respect to design of fiber-based cellular microenvironments.

COLL 598

Adsorption of perdeuterated and protonated proteins at the solid/liquid interface: A neutron reflectivity study

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Neutron reflectivity is a powerful technique for probing adsorbed layers at interfaces. It has been used to investigate proteins adsorbed onto a hydrophilic silica surface. A comparison was made between the protonated and deuterated forms of HSA & MBP. Results show the deuterated proteins to have a higher affinity for the surface with adsorption occurring in a 3:1 ratio when from a 1:1 mixture. Likewise, d-MBP displaces h-MBP more readily than vice versa in an active exchange process. When investigating binary mixtures lysozyme (LYS) dominates when adsorbed from a mixture with h-HSA but from a d-HSA & LYS mix both proteins were adsorbed. The marked difference

between the adsorption of perdeuterated and protonated proteins provides a good case study for testing the neutron reflectivity technique when investigating mixed protein systems. It shows the impact of deuteration on the physicochemical characteristics of the proteins and on the adsorption.

COLL 599

Ceria Nanoparticles as Anti-inflammatory Agent in Engineered Articular Cartilage: *In vitro* Raman Microspectroscopy of Single Cells

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One of the main challenges in repair or recovery of articular cartilage is the sustained inflammatory damage of the cartilage tissue. The adverse effects can, at least partially, be suppressed by administering ceria nanoparticles to the engineered articular tissue constructs. However, the relationships between the mechanical properties and biochemical characteristics of the constructs from one side and intracellular molecular processes from another have been unknown as yet. In this study, we employ *in vitro* Raman microspectroscopy of individual chondrocyte cells in 3D agarose scaffolds to find these relationships. We demonstrate the potential of the method in detecting the molecular changes in chondrocytes during the *in vitro* culture in the presence of inflammatory cytokine (interleukin-1 α) and ceria nanoparticles. We discuss possible mechanisms for the observed beneficial effects of ceria nanoparticles.

COLL 600

Kelvin Probe Force Microscopy (KPFM) study of the conformational change and orientational difference in immobilized Calmodulin (CaM)

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Protein arrays fabrication have been extensively used in the bio-sensing and bio-analysis applications. A key issue in the array technology is to transduce the recognition events to readable signals. In our previous work, 1-Cysteine-mutated calmodulin (CaM) was immobilization on a mercapto-terminated surface through cysteine-Hg-mercapto coupling. Its conformational change was characterized via Atomic Force Microscopy (AFM). In this study, Kelvin Probe Force Microscopy (KPFM), which can measure surface potential variations during a reaction, was utilized to detect the conformational change of CaM to Apo-CaM. Through KPFM characterization, it was also found that the immobilized CaM has two different orientations. This orientational difference might have an influence on the efficiency and robustness of immobilized CaM on a surface. Our

results demonstrated that KPFM was capable of detecting the protein conformational change, as well as probing the protein orientational difference.

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COLL 601

Effective steady shear rheology of a viscous emulsion at finite inertia: Reversal of normal stress differences

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An emulsion of viscous drops in another viscous liquid displays an effectively non-Newtonian viscoelastic rheology. Normally, at creeping flow limit, steady shear rheology of a viscous emulsion shows positive first and negative second effective normal stress differences. Here, we show that in presence of inertia, these normal stress difference changes their signs in a small range of parameters. The emulsion is numerically simulated using front tracking finite difference method, and the effective rheology is computed using volume averaging method using Bachelor's formulation. Both dilute (where drop-drop interaction are neglected) and concentrated (up to 25% volume fraction) emulsions are considered, and results are discussed in detail comparing with analytical theories (Choi-Schowalter and Grmela-Bousmina-Palierne). The unusual rheological behaviors in presence of inertia were physically explained using drop dynamics.

COLL 602

Study of surfactant influence on the low-pH stability of polyolefin dispersions

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Surfactant-free polyolefin dispersions containing ethylene-octene and ethylene-(sodium) acrylate copolymers were created using a mechanical dispersion process. This dispersion has a pH of 10.5 and is stable at room-temperature storage. However, it becomes un-stable with significantly increased viscosity when the pH is lower than 9.5, limiting its applications where a low pH environment is required. The goal of this study was to improve the low-pH dispersion stability through formulation approaches by addition of surfactants. Zeta potential was employed to systematically study the charge densities of different dispersion/surfactant combinations and to predict the colloidal stability. The stability of the polyolefin/surfactant mixtures depends on the surfactant type and concentration. Polyolefin dispersions with the addition of 10 wt% of the

identified surfactants were stable even at the pH of 3.5 without agglomeration and the mixtures have low viscosity. These results suggest that zeta potential measurement is a useful tool to study polyolefin dispersion stability.

COLL 603

Impact of complex surfactant layers at fluid-fluid interfaces on coalescence

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The dynamics of adsorption of single and multicomponent surfactant mixtures at oil-water and air-water interfaces has been characterized using a microtensiometer. The use of microscale interfaces allows the transport processes involved in adsorption to be analyzed and both diffusion and kinetic parameters characterized. The scale of the device allows the bulk solution in contact with the interface to be changed rapidly. We are able to remove the bulk surfactant at different points in during the dynamics of adsorption by rinsing the interface and continuously replacing the bulk fluid with surfactant-free aqueous phase to investigate the reversibility of adsorption. For a bulky nonionic surfactant, Tween-80, a critical interfacial tension arises that links the transport dynamics to the onset of partial reversibility in the system. By measuring the mechanical properties of pre-rinsed and rinsed interfaces, we also find a critical interfacial tension that leads changes in the elasticity of the interfaces. This interfacial tension correlates well with the critical interfacial tension that indicates the onset of partial reversibility. To determine the effects of interfacial elasticity and concentration changes on the stability of an emulsion, we bring two surfactant-coated interfaces into contact and monitor coalescence times and initial droplet shape profiles. We discuss these coalescence results in the context of film drainage, and as drainage time relates to the elasticity of the contacted interfaces. The addition of other surface active species, AOT and rhamnolipid, is also characterized to determine the impact of these surfactants on the reversibility of Tween-80 and on the elasticity of the resulting mixed interfaces.

COLL 604

Maximum bubble pressure rheology of organogels

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Gels are a ubiquitous class of soft materials, where a compound composed primarily of a liquid displays solid-like mechanical behavior due to the addition of a gelator. Many organic solvents are gelled by the addition of small molecule gelators that crystallize in the solution to form a three-dimensional network. Traditional rheological characterization of these gels can be hampered by two factors: first, the practical matter of dealing with measurements using a volatile organic solvent and second, the

brittleness of these gels resulting in failure at low strain amplitudes. This talk will discuss using the technique of maximum bubble pressure rheology to characterize small molecule organogels of 12-hydroxystearic acid in mineral oil. In this measurement an air-filled syringe is used to generate a bubble in the gel. Bubble growth is resisted by the hydrostatic pressure of the solution, the surface tension of the bubble, and viscoelastic resistance of the gel. This results in a maximum pressure during bubble formation, which is related to the mechanical properties of the gel, such as modulus and fracture toughness. It will be shown that this technique can give an accurate measurement of the gel transition temperature and also lends itself well to long-term annealing experiments to study the formation and aging of gels.

COLL 605

Silicone Emulsions

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Silicone emulsions have been finding increasing utilities in a wide range of applications. A patent search in Thomson Reuters' data base (conducted November 6, 2012) using the key word "emulsion" in title/abstract/claims found 22,317 DWPI families among which 2,519 families belonged to silicone emulsions. That is 11%. This talk gives first a brief overview of the basic properties of silicone that make these materials desirable in the many applications, and then touches on the characteristics of silicone emulsions. The second part of the talk focuses on recent understanding of the impact of equilibrium phase behavior on emulsification process using silicone emulsion as an example.

COLL 606

Role of Dispersed versus Solubilized Oil in Aqueous Foam Stability

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Three phase foams (i.e., aqueous foams containing an oil phase) have a variety of practical applications in such areas as enhanced oil recovery, food foams, and in foams containing antifoaming agents. In the present study, we investigated the effects of surfactant micelles and the oil type (polar versus non-polar) in dispersed and solubilized forms on the stability of aqueous foaming systems. The foam stability was studied by the Bartsch test method and the stability of the pseudoemulsion film (that is the film formed between an air-water surface and the surface of the oil drop which is approaching it). In addition, we studied the effect of oil solubilized in the surfactant micelles on foam stability. We measured the second virial coefficient of solutions containing swollen micelles to quantify the micellar interactions. We found that the

relative importance of dispersed oil versus solubilized oil in foam stability largely depends on the stability of the pseudoemulsion film and the second virial coefficient.

COLL 607

Cerato ulmin, how stable is it? Light scattering studies of cylindrical bubbles.

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Cerato ulmin (CU), a class II hydrophobin, has unique properties; specifically, CU forms rod-like bubbles in solution. This is contrary to “normal” spherical bubbles that minimize the surface energy. Optical microscopy studies have shown CU is capable of encapsulating hydrophobic dyes in aqueous solution while keeping the rod-like structures. Microbubbles and nanometer scale structures are also present. While static light scattering experiments have probed the size of these structures in ethanol/water solutions, the stability has not been investigated. In this research, stability of CU in water is observed using dynamic light scattering. Time, temperature, height in the scattering cell and concentration were altered, and the resultant correlation functions were analyzed to explore the stability and size range of structures present. Supported by the Gulf of Mexico Research Institute.

COLL 608

In situ light scattering of shear induced destabilization of emulsion droplets

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A novel system was employed to determine the aggregation behaviour of emulsion droplets in situ while sheared in a rheometer. Tetradecane (15% v/v) emulsions stabilized with 1% sodium caseinate were sheared at various shear rates up to 1000 1/s using a rheometer. The light scattering signal was measured, undiluted using a backscattering geometry. Changes in the viscosity of the emulsions were measured in parallel to light scattering. The colloidal properties after shear were also measured using transmission diffusing wave spectroscopy (with no dilution) and conventional light scattering (after extensive dilution). The set up clearly showed the differences in the flocculation behaviour of the emulsions, induced by addition of calcium or small molecular weight emulsifier, Tween 20. The results demonstrated how measuring changes in situ may help in fine tuning formulations and processes to obtain optimal stability.

COLL 609

Phase behavior and properties of the oil-in-water emulsions stabilized by carboxymethylated and acetylated lignins

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We take advantage of the amphiphilic properties of lignin and its calorific value to develop added value applications in the form of oil-in-water emulsions. Industrial Kraft and organosolv lignins were modified by carboxymethylation and acetylation in order to tune their hydrophilic and hydrophobic characters, respectively. The degree of substitution was controlled by the reaction conditions. The extent of substitution was determined by ¹³C NMR which indicated lignins with various affinities to the aqueous and oil phases as measured by solubility, surface tension, pseudo-CMC, etc. As a proof-of-concept, we used kerosene (equivalent alkyl carbon number of 12) as the oil phase. The salinity and pH of the aqueous phase were varied as formulation variables in different Winsor types of systems which were emulsified using standard protocols. We relate the results from phase behavior to the nature and stability of the emulsions in O:W ratios ranging from 2:8 to 8:2.

COLL 610

Ostwald ripening of nanoparticle systems

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Ostwald Ripening, the interfacial-energy-driven dissolution and re-precipitation of solutes, becomes a significant problem for the stability of nanoparticle formulations. At nanometer length scales interfacial energy and curvature become significant relative to bulk solubility. While the phenomenon is known to be important, we present the first quantitative study of Ostwald ripening for nanoparticle dispersions. The Lifshitz, Slyozov and Wagner (LSW) theory of particle growth driven by diffusion is applied to study β -carotene-loaded nanoparticles with sizes of O(100 nm) formed by our block-copolymer protected Flash NanoPrecipitation process. A numerical implementation of the theory that accounts for the original particle size distribution is presented. As parameters, the model requires: the bulk solubility and diffusion coefficient of the solute, interfacial tension between the dispersed phase and solvent, and the initial particle size distribution. These parameters are all independently measured. The predicted particle sizes from the numerical simulation are compared with the experimental results measured by Dynamic Light Scattering (DLS). The results show quantitative agreement with no adjustable parameters. The addition of anti-solvent results in the reduction of the ripening rate by dramatically decreasing bulk solubility. A 40 fold decrease in the bulk solubility is shown to reduce the initial rate of particle growth 10 fold.

COLL 611

Simulations of micellization of ionic surfactants

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This presentation focuses on self-assembly of ionic surfactant into micelles, using molecular simulation methods. We have developed implicit-solvent ionic surfactant models and have used them in Grand Canonical Monte Carlo simulations to investigate the critical micelle concentration, aggregation number and micellar shape in the presence of explicit salt. Explicit-solvent models have also been studied, using GPU computing to reach the microsecond time scales necessary for equilibration. We present evidence that the free surfactant concentration is much lower than the cmc for strongly micellizing systems at the relatively high concentrations accessible by simulations. Thus, one must account for counterion association and extrapolate with respect to overall surfactant concentration when determining the CMC from the raw simulation data.

COLL 612

Understanding structural transitions in micelles through molecular simulations

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Surfactants are important interfacial agents in many biological and industrial systems. Their self-assembly and versatility of the aggregates lies at the heart of all biological membrane, vesicle and micelle formation, and many industrial solubilization processes. While biologically and industrially extremely important, surprisingly little is known about molecular details of the self-assembly of surfactants and the dynamics of the formed structures. In this talk, I present the results of our detailed molecular dynamics simulations on micellar aggregate structure and dynamics. In particular, I concentrate on structural transitions driven by ionic strength of the solution. The results include detailed description of anionic micelle fission, packing and unpacking (structural changes) in the micelles brought forth by differences in the ionic strength of the solution, and surfactant structure dependent control of micellar surface coatings for aqueous dispersion.

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COLL 613

Molecular simulations of surfactant micellization: A direct comparison with scattering experiments

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The modeling of self-assembly phenomena of amphiphilic molecules through molecular simulations is a challenging task due to the long time scales ($>1\mu\text{s}$) and low critical micelle concentrations (cmc) that typically lie below 10mM. A recently developed implicit solvent surfactant model allows to overcome these problems. It will be demonstrated that the model yields realistic results in terms of the cmc and the aggregate size for various ionic and non-ionic surfactant types. A particular focus lies on structural correlations of micelles. Scattering intensities of micelles consisting of trimethyltetradecylammonium bromide (TTAB) surfactants are calculated and directly compared with data obtained from anomalous small-angle X-ray scattering experiments utilizing synchrotron radiation facilities. The simulations reveal fluctuation effects of micelles mainly caused by the counterions. The TTAB study provides an excellent show case for the capability of combining molecular simulations and scattering experiments to properly analyze shape and correlation properties of self-assembling amphiphilic compounds.

COLL 614

Hydrophobic interactions between Sodium dodecyl Sulfate surfactants and Polyethylene Oxide (PEO) and Polyvinyl Pyrrolidone (PVP) Studied by Molecular Dynamics Simulations

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We analyze and compare the polymer-surfactant aggregation phenomenon by looking at the interactions between the anionic sodium dodecyl sulfate (SDS) surfactant and two non-ionic polymers – poly-(ethylene oxide) (PEO) and poly-(vinylpyrrolidone) (PVP). We simulated a 64 monomer SDS micelle along with 30 monomers of PEO and PVP chains solvated in water molecules. In both cases the polymer chain adsorbs on the hydrophobic regions of the SDS micelle surface supporting the beaded necklace model. The association of hydrophobic regions in the polymer and micelle suggest that the hydrophobic effect is the driving force for association. The sulfur-sulfur radial distribution function plots for neat SDS, SDS+PEO, SDS+PVP systems shows that the headgroups are more tightly packed upon saturation of the micelle. We also focus on studying the

effect of temperature on the micellar properties of SDS in the presence of PEO and PVP in the temperature range of 270-370K.

COLL 615

Molecular mechanisms of micelle-nanoparticle complex formation

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Self-assembly of metal nanoparticles with cationic cylindrical surfactant micelles is known to produce stable nanogels with tunable optical properties [1]. Coarse Grained Molecular Dynamics simulations based on methodologies developed recently [2-4] are performed to explore the molecular mechanism underlying this self-assembly process. It is observed that nanoparticles encapsulated in a surfactant corona or vesicle are capable of forming stable junctions with cylindrical micelles primarily through an end cap opening mechanism. The energetics of the micelle-nanoparticle bridging process and the effect of flow shear on the stability of the bridges will be discussed.

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COLL 616

Tablet-Shaped Micelles: A Novel Approach to Rationalize the Growth Behavior of Surfactant Micelles

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The conventional view on surfactant micellar growth considers the micelles as small spheres that grow exclusively in the length direction to form spherocylindrical micelles. The spherocylindrical model predicts that all surfactants show a more or less identical growth behavior with respect to surfactant concentration. Such behavior is, however, not consistent with experimental results. For instance, Gemini surfactants with a short spacer group frequently show a considerable growth behavior, with the aggregation number nearly proportional to surfactant concentration, whereas Gemini surfactants

with a longer spacer group change aggregation number only slightly with concentration. On the other hand, the different growth behaviors may be rationalized by means of considering the micelles shaped as triaxial tablets. According to this view, micelles that grow almost exclusively in the length direction may change aggregation number considerably whereas micelles that grow with respect to both width and length display a more modest change of aggregation number.

COLL 617

Micelle Breakdown via a Fusion Mechanism

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The classical model for breakdown of surfactant micelles involves the sequential loss of individual monomers from the micelle and is governed by a set of equations known as the Becker-Döring equations. Calculations of the breakdown rate of non-ionic micelles of the family C_nE_m yield micelle lifetimes many orders of magnitude longer than those observed experimentally. An alternative model for micelle breakdown is presented that involves the fusion of micelles to form a 'supermicelle' followed by sequential monomer loss to regenerate a single 'proper' micelle. A single mathematical model has been developed that incorporates the Becker-Döring mechanism as a subset of the model and the conditions under which micelle fusion plays an important role is evaluated.

COLL 618

Key Features of TiO₂-based Nano-architectures for CO₂ Conversion

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The global potential of solar energy is vast, but we currently tap only minor amounts to meet our ever-growing energy demand. Photocatalytic conversion of radiant to chemical energy provides a variety of possibilities for local, off-the-grid energy. The major obstacle, however, is the lack of catalysts that can efficiently couple abundant solar energy with a reducing agent such as water to cleave the C-O bonds in CO₂ and form C-H bonds in products. Ideally, this goal requires a multifunctional catalyst that can separate the many functions of light harvesting, charge separation, and CO₂ activation to facilitate proton coupled electron transfer to produce high-energy products selectively. A variety of TiO₂-based nanocomposite materials have been synthesized and characterized to reveal salient structural and chemical features (e.g., reduced metal centers, oxygen vacancies, preferred crystal facet orientation, undercoordinated surface sites, various interfacial geometries) critical to tackling the many challenges of artificial photosynthesis.

COLL 619

Photocatalytic Conversion of CO₂ in Water over Layered Double Hydroxides (LDHs)

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Conversion of the greenhouse gas CO₂ into carbon and useful carbon sources such as CO, HCOOH, HCHO, CH₃OH, and CH₄ is a potential method of solving energy and environmental problems. Photocatalytic conversion of manmade CO₂ is attractive from the viewpoint of sustainable energy production and greenhouse gas reduction. Our group found that CO is generated in the photocatalytic conversion of CO₂ over ZrO₂, MgO, ATaO₃ (A = Li, Na, and K), and Ga₂O₃, which have the properties of solid base catalysts, in the presence of H₂ or CH₄ (reductant). CO₂ can be adsorbed on a solid base, indicating that solid bases determine, alter, and control the structure of CO₂ on their surface. However, these oxides did not function as a photocatalyst in water. Layered double hydroxides (LDH) are synthetic or natural crystalline clays that consist of brucite (Mg(OH)₂)-like positively charged two-dimensional sheets in which some divalent cations such as Mg²⁺ are substituted by trivalent cations; further, water and exchangeable charge-compensating anions are present in the interlayer. Mg-Al LDH catalyzes the aldol reaction of carbonyl compounds in aqueous solution because of the high water tolerance of the surface base sites. In this study, we carried out the photocatalytic conversion of CO₂ in water in the presence of various LDHs. Considerable amounts of CO and O₂, which were probably derived from CO₂ and H₂O, were obtained in the photocatalytic conversion of CO₂ over various LDHs in water, but a simple metal hydroxide, which has the constituent elements of the LDH, showed low activity for CO and O₂ evolution.

COLL 620

Operando and in-situ studies of bimetallic catalysts

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Bimetallic catalysts play important roles in chemical transformation and energy conversion processes. Bimetallic nanocatalysts such as Pd-Zn and Ni-Ga with a single phase were prepared. Catalytic performances of Pd-Zn and Ni-Ga catalysts with different compositions for production of hydrogen from methanol were measured. A composition-dependent catalytic selectivity was revealed in these alloy catalysts. Operando studies identified their active surface composition at different reaction conditions. A correlation between surface chemistries and their catalytic performances was built. In addition, CO oxidation on Pd-Cu and Pt-Cu nanocatalysts with well controlled composition and structure were studied. Operando studies of surface

composition of different Pd-Cu and Pt-Cu catalysts shows that tuning surface composition can optimize catalytic performances in CO oxidation.

COLL 621

Tailoring Cu valence and oxygen vacancy in Cu/TiO₂ nanocomposites for enhanced CO₂ activation and photoreduction

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The incorporation of Cu species in TiO₂ photocatalysts is very beneficial in photocatalytic CO₂ reduction to fuels, but the effect of Cu valence is not clear. When preparing reduced Cu species on TiO₂ in a reductive atmosphere, surface defects such as oxygen vacancies may be created concurrently. However, no work has investigated the potential synergies between Cu and the defects on TiO₂ for CO₂ activation and photoreduction. In this research, we fabricated defective Cu/TiO_{2-x} nanocomposites with tailored Cu species (Cu²⁺, Cu⁺, or Cu⁺/Cu⁰ mixture) through thermal treatment in H₂ or He environment. We measured the rates of CO₂ reduction and correlated the catalytic activity with reaction intermediates observed from in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). It was found that Cu/TiO₂ with a defect-dominated surface exhibited much higher activity than that with a defect-free surface. CO₂⁻ species, generated upon an electron attachment to CO₂, are spontaneously dissociated into CO on defective Cu⁺/TiO_{2-x} at room temperature even in the dark. This dissociation process is to a large extent associated with the surface oxygen vacancies that provide not only an electronic charge (Ti³⁺), but also the sites for the adsorption of oxygen atoms from CO₂. In addition, the mixture of Cu⁺/Cu⁰ induced by H₂-reduction seemed to be more active in charge separation than Cu⁺ species alone induced by He-pretreatment, thus resulting in a higher activity for CO₂ photoreduction. The surface chemistry explored is of great significance to the design of efficient photocatalyst and to the understanding of CO₂ reduction mechanism.

COLL 622

New Strategies for the Catalytic Reduction of CO₂

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Various strategies for the photoreduction of carbon dioxide will be presented.

1. Reduction with hydrogen. A phenanthroline ligand decorated at the 5,6 position with a 15-crown-5 ether was used to prepare a metallorganic-polyoxometalate hybrid complex Re^I(L)(CO)₃CH₃CN-MH₂PW₁₂O₄₀ (L = 15-crown-5-phenanthroline, M = Na⁺, H₃O⁺). X-ray diffraction, ¹H and ¹³C NMR, ESI-MS, IR and elemental analysis were used to characterize this complex. In the presence of Pt/C, the polyoxometalate moiety in Re^I(L

$(\text{CO})_3\text{CH}_3\text{CN}-\text{MH}_2\text{PW}_{12}\text{O}_{40}$ can oxidize H_2 to two protons and two electrons which in the presence of visible light can catalyze the photoreduction of CO_2 to CO with H_2 as the reducing agent instead of the universally used amines as sacrificial reducing agents. An EPR spectrum of a stable intermediate species under reaction conditions shows characteristics of a $\text{PW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}$ and a Re^0 species with a tentative assignment of the intermediate as $\text{Re}^0(\text{L})(\text{CO})_3(\text{S})-\text{MH}_3\text{PW}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}$.

2. Reduction with water. A similar hybrid compound based on a ruthenium(II) bipyridine complex decorated with a crown ether that complexes the photoactive $\text{PW}_{12}\text{O}_{40}^{3-}$ polyoxometalate was prepared. Support of this compound onto a titanium-silicate support allowed the photoreduction of CO_2 to CO with UV light.

3. Photocatalytic splitting. As prelude to the possibility of photocleavage of CO_2 to its components, CO and O_2 , the catalytic photocleavage of isostructural CS_2 to S_8 and a $(\text{C}_x\text{S}_y)_n$ polymer with visible light was studied. A dinuclear ruthenium(II) compound with a bipyridine units for photoactivity and a vicinal tertiary amine binding site for improved CS_2 activation was prepared and characterized by X-ray diffraction, ^1H NMR, ^{13}C NMR, ESI-MS and elemental analysis. A significant amount of CS_2 underwent a photocleavage reaction (220 turnovers, 20 h) to yield isolable S_8 and a $(\text{C}_x\text{S}_y)_n$ polymer. A mononuclear catalyst or one without an amine binding site showed significantly less activity.

COLL 623

Enhanced Photocatalytic Reduction of CO_2 to Hydrocarbon Fuels via Plasmon-Enhanced Absorption

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We present a systematic study of mechanisms of Au nanoparticle/photocatalytic semiconductor-catalyzed photoreduction of CO_2 and water vapor over a wide range of wavelengths (254nm, 365nm, 532nm, 633nm). When the photon energy matches the plasmon resonance of the Au nanoparticles (free carrier absorption), we observe a significant enhancement in the photocatalytic activity due to the intense local electromagnetic fields created by the surface plasmons of the Au nanoparticles. These intense electromagnetic fields enhance absorption in the photocatalytic semiconductor, thereby enhancing the photocatalytic activity in the visible range. We use $^{13}\text{CO}_2$ isotopes in order to verify the origin of carbonaceous species (i.e., CH_4) produced by the catalytic process. We model the plasmon excitation at the Au nanoparticle-photocatalytic semiconductor interface using finite difference time domain (FDTD) simulations, which provide a rigorous analysis of the electric fields and charge at the interface.

COLL 624

Heterostructured photocatalysts for efficient visible light CO₂ conversion

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As the evidence of global climate change becomes ubiquitous, there is a pressing need to mitigate the negative impacts of fossil energy consumption, of which CO₂ emission is the major concern. Photocatalytic reduction of CO₂ offers a promising solution because it not only reduces the amount of CO₂ released to the atmosphere, but also converts the green house gas into useful chemicals and fuels, such as methane, CO, methanol, etc. Despite the great promise of this strategy, the artificial photocatalytic CO₂ reduction is highly inefficient and impractical. One of the challenges is that metal oxide based photocatalysts are incapable of utilizing visible and near infrared photons for photocatalysis. We have developed various heterostructured photocatalysts which exploit the attractive optical properties of semiconductor and metal nanocrystals to sensitize wide band-gap metal oxide catalysts. These heterostructured photocatalysts have shown CO₂ reduction activity deep into the red tails of the visible spectral region. Mechanisms of different types of heterostructured photocatalysts will be discussed. Our most recent effort in developing methods for plasmon-assisted photocatalysis applications will also be described.

COLL 625

Detection of drug-membrane and drug-protein interactions via surface second harmonic imaging and spectroscopy

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Drug-membrane interactions play a crucial role in the pharmacology and biological activity of drugs. The equilibrium of a drug molecule between plasma and the cellular membrane has historically been modeled by bulk phase partitioning, usually between water and 1-octanol. On a fundamental level, the thermodynamics of a lipid membrane, which is comprised of a bilayer of lipids ~50Å thick, cannot adequately be modeled by the bulk thermodynamic properties of a homogenous liquid phase. The measurement of drug association to lipid membranes has conventionally been measured by fluorescence and other spectroscopic methods. However, a main disadvantage of fluorescence labeling of drugs is that the introduction of fluorophores will change the molecules physical properties, such as charge, hydrophobic or hydrophilic character and structure. To circumvent these problems, we have developed a novel form of second-harmonic (SH) microscopy in conjunction with 2-D lipid bilayer arrays for the high-throughput, ultra-sensitive and label-free detection of small-molecule drug association to lipid membranes.

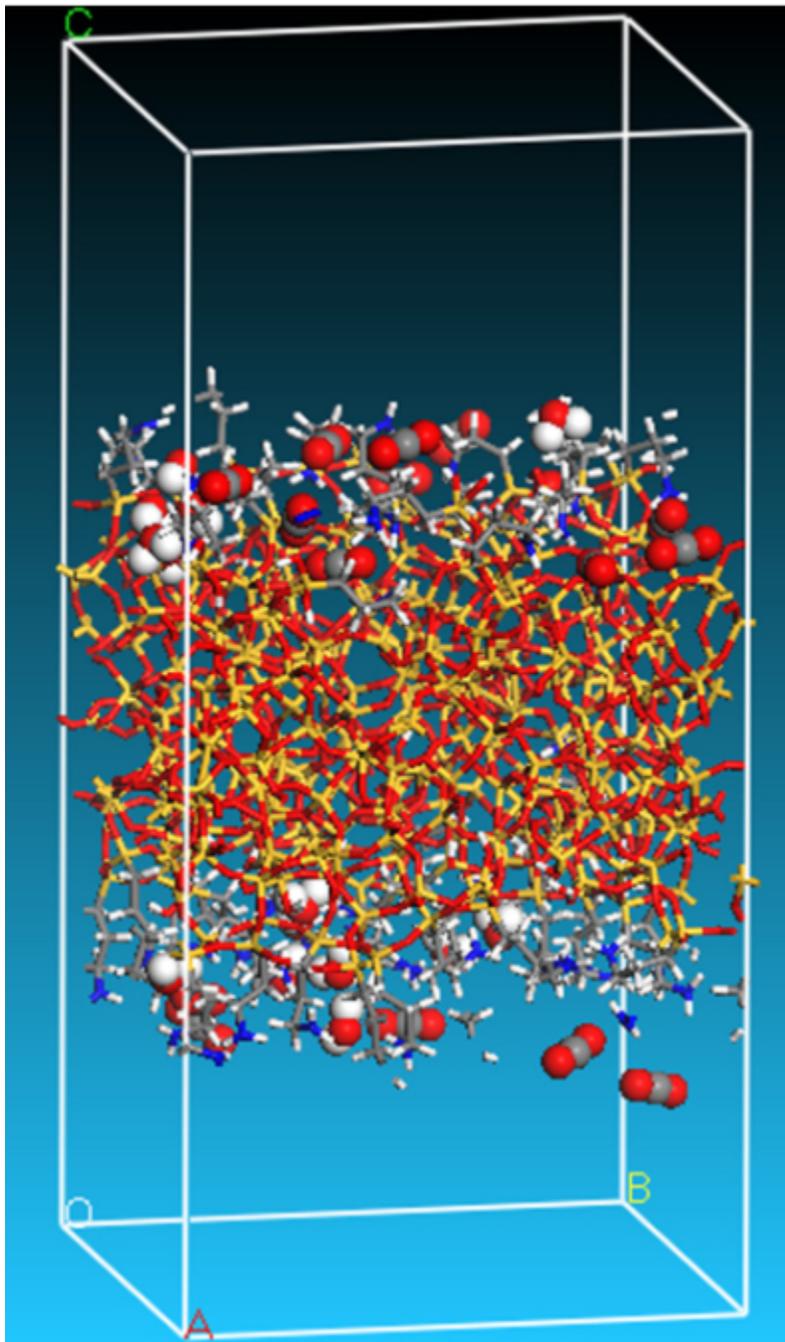
COLL 626

Interaction of carbon dioxide and water with amine-grafted silica surface: a molecular modeling study

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Using a combination of classical and ab initio modeling methods, we study adsorption of carbon dioxide on amorphous silica grafted with propylamine chains at moist conditions that may be found in post-combustion gases. We constructed a 3nm thick hydrophilic silica slab that represents a solid wall separating pores of mesoporous siliceous materials. Then the surfaces were grafted with amine groups and surface heterogeneity was characterized through adsorption of argon, carbon dioxide and water, which serve as a standard probe molecules.

With the model constructed, we explored the mechanisms of sorption and diffusion of carbon dioxide and water. We model physisorption and chemisorption aspect separately, using classical and ab initio tools, respectively, and consider different sorption mechanisms leading to formation either carbamates or bicarbonates. Carbamate formation requires two, and bicarbonate one amine groups per CO₂ molecule. We assumed that chemisorption mechanism depends on both (1) energies and barriers of CO₂ reaction with the grafted amines and water (2) typical molecular arrangements of the reactants at the surface that may trigger a particular reaction scenario, since the initial states for carbamate and bicarbonate are different. Our simulation predict that carbamate formation is preferential from both physisorption and chemisorption point of view. Bicarbonate scenario may be favorable only at high level of water sorption, which, as our analysis of published experimental data shows, is hardly achievable at practical conditions on amine-doped silica.



COLL 627

Connecting structural defects and optical properties of core-shell Quantum Dots induced by interfacial lattice strain

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Type I core-shell quantum dots are continuing to receive great interest due to their superior optical properties compared to other types of fluorophores. High quantum yields and high photostability are easily achievable when the core material is coated with a higher-bandgap shell material which confines the excitons to the core and decreases charge carrier trapping at the surface. However, the shell material shows different lattice parameters from the core, thereby introducing interfacial lattice strain, which depends on both the material and its thickness. Furthermore, the interfacial lattice strain may cause the shell to grow anisotropically, so that controlling the distribution of the shell material around the core remains a challenge. Successive ion layer adsorption and reaction (SILAR) has helped to alleviate these problems, however, the exact details of the shell growth are still far from understood. To address this, we have synthesized various core-shell and core-shell-shell quantum dots (e.g. CdSe/ZnS, CdSe/CdS, CdSe/CdS/ZnS) and analyzed both their optical and structural properties as a function of the shell thickness. By analyzing HR-TEM images and HAADF-STEM coupled with electron energy loss spectroscopy (EELS), we report on the effect of the interfacial lattice strain on their optical and structural properties, such as quantum yield, fluorescence lifetime, blinking, and shell distribution. These results are used to draw connections between structural defects and charge carrier relaxation pathways.

COLL 628

Geometry of colloidal crystals

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Inverse opal structures are highly ordered, porous materials traditionally formed from backfilling a colloidal crystal with an inorganic material. Our lab has developed a method to form crack-free inverse opals with homogeneous crystal orientation over large areas by following a co-assembly strategy to crystallize polymer colloids in the presence of silica-precursors [Hatton et al. *PNAS* 2010]. Due to their high periodicity, these materials behave as three-dimensional photonic crystals with interesting optical properties that depend on the size and symmetry of the pores. Likewise, the wetting of such porous, ordered materials depends on the geometry of the pores and the surface chemistry of the inverse opal. We have shown that tuning of the latter using silane chemistry can be used to tailor the wetting properties, leading to the creation of a colorimetric sensing platform [Burgess et al. *JACS* 2011]. In this contribution, we focus on the effects of size and geometry of the pores on the intrinsic properties of inverse opals. While the size can be tuned by changing the initial colloid size, the geometry of the pores can be tuned from spherical to elliptical by changing the annealing

temperature. We show that the geometry of the pores has profound effects on the intrinsic properties of the inverse opals.

COLL 629

Molecular dynamics study of mixtures of alcohol polyoxyethylene ether carboxylate/ alcohol polyoxyethylene ether at the air/water interface

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Dynamic diffusion behaviors of surfactants mixtures containing alcohol polyoxyethylene ether carboxylate (AEC) and alcohol polyoxyethylene ether (AEO) with molar ratio of 70:30 from solution to interface are investigated by atomistic MD simulation. Surfactants diffusion process, the adsorption amount and the monolayer structure are considered. It has been observed that the adsorption goes through “surfactants dissolving—formation of pre-micelles in subsurface—surfactants monolayer” process. However, the pre-micelles are so ephemeral that they only exist in the period of the magnitude of 10^{-11} second, making them too difficult to be detected experimentally. In addition, the surfactants adsorption ratio at interfaces is independent of surfactant concentration, although AEO diffuses faster. When adsorbed at interface, AEO molecules arrange far from each other with all hydrogen bonds formed combined with AEC. Compared with AEO configuration, AEC head_groups penetrated more into the water phase and twisted, while tail_chains stretched and ordered.

COLL 630

Investigation of dispersive interactions of cellulose, lignin and glucomannan by spectroscopic ellipsometry

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Dispersive interactions between the different components, of for example the wood cell wall, are strongly influencing the combined material properties. This investigation concerns these interactions between lignin, hemicellulose and cellulose, materials highly abundant in natural materials such as plants and trees. Spectroscopic ellipsometry has been used to estimate spectral parameters in the visible-ultraviolet region of well-defined model surfaces of pure lignin and glucomannan. These parameters were then utilized to calculate the non-retarded Hamaker constant in water and vacuum using the Lifshitz theory. In vacuum, the Hamaker constants of lignin and

glucomannan were calculated to 46zJ and 35zJ respectively. These Hamaker constants, for glucomannan and lignin, and previously reported values for cellulose, were used to evaluate the dispersive interactions between cellulose, glucomannan and lignin, both in water and vacuum. The spectral data have also been used to compare the dielectric response and the energies associated with the characteristic frequencies in the UV-range.

COLL 631

Correlating contact electrification with chemical structure in liquid electrets

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The accumulation of electrostatic charge on materials via contact electrification (tribocharging) is important for processes as varied as xerography and the separation of waste for recycling. Although contact electrification is ubiquitous, the molecular processes by which it occurs are still not well understood. This talk will describe the charging of liquids flowing through capillaries and show that it is consistent with the triboelectric series for solid materials. Calculated energies of neutral, charged, and radical species will indicate possible chemical intermediates, products, and mechanisms of tribocharging. This experimental and computational study is designed to understand the relationship between contact electrification and chemical structure, which is necessary to harness or control contact electrification in general.

COLL 632

AFM transverse shear as a probe of crystallinity at the interface of gate insulator and organic semiconductor

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Crystalline structure is critical to the performance of many organic thin film devices, especially the first molecular layers on the gate of a field effect transistor. The ideal probe of crystallinity is surface sensitive (of film growth stopped at different stages) and real-space in character, to reveal possibly complex structures in-plane. In this presentation we present new methodologies that use shear forces in atomic force microscopy (AFM) to provide this sensitivity. We have developed an understanding of shear forces sensed *perpendicular* to the AFM fast-scan direction. It has a different physical origin than frictional forces, as seen in a lack of rate and temperature dependence. A shear deformation model establishes a connection to the in-plane elastic modulus *tensor*. A mosaic of first-monolayer pentacene grains is revealed by

TSM. Quantitative force analysis identifies each grain's crystallographic orientation. A rotational epitaxy between first and second monolayers of pentacene is revealed.

COLL 633

Heat Transport through Monolayers at Solid–Liquid Interfaces

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Recent work has shown that changes as minor as a few atoms in a monolayer of material at an interface can significantly alter the measured heat conductance through an interface. Thus, the addition of thin organic films should be able to control heat conduction in situations where there is a high density of interfaces, such as nanoparticle dispersions or in micromachines. Here we report measurements of the interface conductance of some gold-thiol-water interfaces that show how the omega group of a self-assembled monolayer affects heat conductance. These measurements were performed using Time-Domain Thermoreflectance. We find that interface conduction increases with decreasing water contact angle and is a function of the salt concentration in water. Thus interface conductance can also be used as a probe to study the nature of interfaces.

COLL 634

Using conductance to characterize surface-coated, single-molecule nanopore sensor interfaces

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Nanopores are molecular-scale holes in insulating membranes that can be adapted to a number of single-molecule sensing, characterization and manipulation schemes. Most frequently, nanopore membranes are immersed in electrolyte solutions and the passage of analyte molecules through the typical <10nm pore diameter and <100nm length is detected through perturbations of the ionic current through the pore. On this length scale, the size, shape and surface chemistry of the nanopore are key determinants of the performance of nanopore methods. These factors dictate the feasible experimental implementation, and determine the signal and the likelihood of molecular interactions at the constrained nanopore-solution interface. The conductance of a nanopore can be used as a sensitive probe of both nanopore geometry and surface chemistry, and we present results in which conductance changes following nanopore surface chemical modification can be used to characterize the structure and chemistry of this interface.

COLL 635

Molecular structures of proteins and peptides at interfaces

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Molecular structures of proteins and peptides at interfaces play important roles in biocompatibility, performance of marine anti-fouling coatings, membrane protein functions, and antimicrobial activity and selectivity. Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular structures of peptides and proteins in different interfacial environments, e.g., in model cell membranes or chemically immobilized onto solid substrates, supplemented by attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR). Peptides with different secondary structures including alpha helix, 3-10 helix, and beta-sheet were studied. SFG and ATR-FTIR have been successfully applied to investigate membrane orientation of various proteins and conformations/orientations of chemically immobilized enzymes.

COLL 636

Electrochemical and Surface Plasmon Resonance Imaging Based Investigation of Barnacle Adhesion

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The mechanism by which barnacles adhere to surfaces is unresolved. Different lines of evidence support a mechanism by which multiple liquid fractions secreted at the advancing leading edge of the base plate react to form a solid adhesive. Here we describe results in which electrochemical techniques and surface plasmon resonance imaging are applied to investigate adhesion of *Balanus amphitrite* to a gold surface. The results reveal an abrupt ennoblement by which the open circuit potential of the gold surface increases dramatically following resettlement of a barnacle. This ennoblement appears associated with the readhesion process and suggests possible redox activity of one more of the secreted fractions. The results also reveal peristaltic-like pumping of a liquid fraction along the base plate leading edge. Such pumping is consistent with recent confocal microscopy that revealed periodic secretion of liquid fractions along the base plate leading edge.

COLL 637

Changing morphology of functional amyloid structures

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“Functional” amyloids are self-assembled protein materials that appear in barnacle cement, bacterial hyphae, fungal spore coatings, and insect silks and are meant to proliferate life. Functional amyloid morphology can vary from fibrous to globular. Barnacle cement has been shown to be a mixture of globules and fibers depending on substrate surface energy and environmental conditions. This implies that the organism reacts to its environment to produce materials with different properties to meet the demands of the new living conditions. It is hypothesized that functional amyloids form from protein mixtures meeting defined “template” and “adder” properties. These peptides contain “molecular switches” that can be activated by concentration fluctuations. Here, an *in vitro* functional amyloid system is compared to *Megabalanus rosa* proteins to show that *M. rosa* proteins have template and adder properties and that the morphology of the *in vitro* system can be altered with concentration fluctuations that activate molecular switches.

COLL 638

Biochemical variations in the tree ring-like growth patterns of barnacle adhesive interfaces

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Barnacles are notorious marine foulants that adhere to submerged surfaces with surprising tenacity. The adhesion process is complex, involving multiple physiological processes and timed secretions. Previous biochemical analyses of barnacle cement have primarily focused on the bulk cement. However, barnacle cement contains a series of concentric circles that are commonly observed in optical, epifluorescent, and confocal microscopy, suggesting the composition of the adhesive may vary on a microscopic scale. To explore the heterogeneity of barnacle cement, the adhesive plaques of multiple barnacles were examined with several high spatial resolution techniques, including optical, epifluorescent, confocal, and infrared (IR) absorption microscopy, as well as X-ray photoelectron spectroscopy and atomic force microscopy. Using IR absorption microscopy, a technique sensitive to local changes in chemical composition, we have observed a non-uniform distribution of multiple chemical species in radial patterns that coincide with visible and autofluorescent features in the barnacle cement. The IR spectra also show significant chemical changes near secretory structures at the adhesive interface. We found substantial shifts in the Amide I band, suggesting that the secondary structure of proteins is not constant throughout the cement. Specific vibrations corresponding to phenolic compounds and polysaccharides were also found

in variable intensities. Analysis of these data reveals distinct chemical differences that vary both radially and perpendicular to the substrate, providing insight to the construction of the barnacle adhesive interface.

COLL 639

Characterizing the protein-surface interactions that control diatom biomineralization

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The formation of silica-based cell walls in marine, single celled organisms, is regulated by protein–mineral interactions. The diatom species *Cylindrotheca fusiformis* assembles supermolecular silica structures via proteins called sillafins. In a silicic acid solution, specific repeat units within this protein, SSKKSGSYSGSKGSKRRIL (R5), induce the formation of silica-protein composite nanoparticles. The protein–surface interaction that drives self-assembly is likely controlled by specific contacts between the surface atoms and key protein side chains. In this study, we characterized this R5-SiO₂ interaction by both near edge x-ray absorption fine structure (NEXAFS) spectroscopy and *in situ* sum frequency generation (SFG) spectroscopy. Two peaks within the amide I vibrational band of the SFG spectra, 1640 and 1670 cm⁻¹, indicate that the R5 peptide retains a beta sheet conformation when interacting with SiO₂. While details of the binding geometry of the single tyrosine within R5 is provided by the observed polarization dependence of the NEXAFS C1s to π* transition related to the tyrosine's phenyl ring.

COLL 640

Protein Melts: Examples from Nature and Applications in Materials Coatings

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We report the reversible melting of a natural protein complex, which is based on a process that breaks down the bonds of inter-domain interactions of the protein complex in the presence of water and heat. Synthetic protein melts have been reported earlier, but the liquid phase for macromolecules is rare in nature because the protein domain size is larger than the range of the attractive interactions such as van der Waals. We studied the melting process by dynamic mechanical analysis (DMA) and Raman spectroscopy. Sequencing studies and comparative modeling showed that the protein complex is made of β-sheet domains. The DMA showed that the protein is stable at dry conditions, but starts to flow even at room temperature in wet conditions. Raman studies in wet conditions showed that number and size of the crystalline domains made of β-sheets do not decrease even at elevated temperatures. This unique property

makes the melting of the protein complex reversible, which opens up applications as novel nanomaterials and surface coatings.

COLL 641

Effect of PEGylated lipids on lipid-based nanodisc-to-nanovesicle mechanism

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Lipid-based nanodiscs can be found in mixtures composed of two or more immiscible lipid species with significantly different spontaneous curvatures. Generally speaking, nanodiscs can be synthesized by mixing a gel-phase long-chain lipid and an α -phase short-chain lipid. Upon elevation of temperature, these nanodiscs are transformed into nano-vesicles due to the increased miscibility among the species as the gel-phase long-chain lipid starts to melt. It has been reported that up to 5 mole% of PEGylated lipid can be incorporated into the nanodiscs. As a result of their steric interactions, PEGylated lipids can presumably affect the disc-to-vesicle transition. In this presentation, we will present a study on the disc-to-vesicle transition in a system composed of dipalmitoyl phosphatidylcholine (DPPC) and dihexanoyl phosphatidylcholine (DHPC), doped with a small amount of dipalmitoyl phosphatidylglycerol (DPPG). PEGylated lipids of different PEG molecular weights are incorporated in the mixture and then, the transition is monitored through dynamic light scattering. The effect of molecular weight and molar ratio of PEGylated lipids on the structural transition will be reported.

COLL 642

Tension selects between membrane transitions resulting in striped or hexagonal domains

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Because of the importance of phospholipid rafts in cellular function and because of the utility of phospholipid membranes to probe phase transitions in confinement, transitions in phosphatidyl choline bilayers have long been a topic of interest. Investigations of phase behavior often map the phase diagram in temperature-composition space, for 2 or 3 component systems. When it comes to cell function, however, tension could be at least as important: At fixed physiological temperature, cell functions regulate tension at least as high as 0.4 mN/m. We report here the impact of tension on two-component phosphatidyl choline membranes. While there is a general effect for elevated tensions to suppress phase separation as a result of the greater areal density of the solid phase, this happens in complicated ways, more dramatic than the calculated effects from Clausius Clapeyron. Instead of the mere 0.3 C suppression of the phase separation

temperature for each mN/m of applied tension, we report a dramatic change in the nature of the solid phases from patches / hexagon at low tensions to stripes at high tension, where the latter can selectively incorporate some tracers while the former do not. We explain this effect based on a calculated triple point near the temperature range of interest.

COLL 643

Real-time Visualization of Membrane Remodeling following Physical-chemical perturbations

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Giant unilamellar vesicles (GUVs) – microscopic compartments outlined by semi-permeable elastic membranes consisting of phospholipid bilayers – isolate their encapsulated aqueous core from the surrounding bulk water. They can be readily prepared by electroformation or hydration to achieve sizes in the range of tens of micrometers from pre-determined molecular components and with known concentration gradients, thus GUVs provide an ideal platform for real-time characterization of extraneously stimulated membrane remodeling by optical fluorescence microscopy. We present our preliminary observations of membrane remodeling induced by the introduction of (1) osmotic gradients across the vesicle compartment; (2) membrane-partitioning amphiphiles (e.g., MSDH, O-methyl-serine dodecylamide hydrochloride); and (3) lipid-binding proteins (e.g., Annexin V). The diverse range of response includes shape deformation, budding, and rupture, all of which can be explained in terms of an interplay between membrane tension, curvature, and phase behavior.

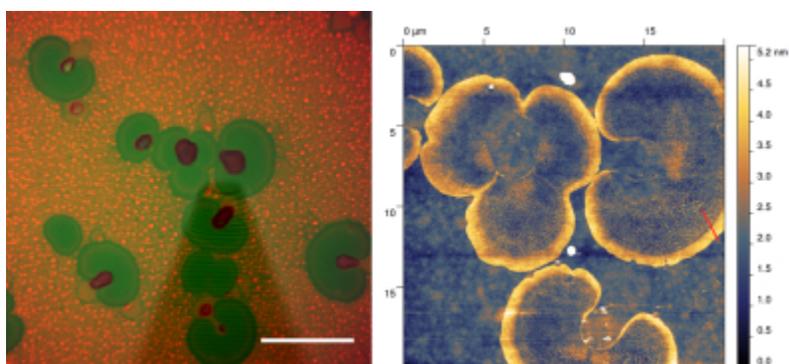
COLL 644

Squalene's role in the formation and organization of membrane domains of *Halobacterium salinarum*

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In the work reported here, we compare two physical-chemical characteristics, namely the interfacial compressibility and lateral organization (both influenced pronouncedly by cholesterol in mammalian cells) of squalene containing (total) and squalene devoid (polar) lipid extract of *Halobacterium salinarum* NRC-1. Pressure-area isotherms derived from Langmuir experiments map onto other classical amphiphiles and reveal packing characteristics and elastic compressibility properties to be strongly modulated by the presence of squalene in the total lipid extract: the incorporation of squalene dramatically extends elastic area compressibility and allows for tighter packing of archaeal lipid mixtures. Squalene also appears to influence lateral organization of archaeal membrane components. Epifluorescence and atomic force microscopy based characterization of Langmuir monolayers transferred onto solid hydrophilic reveal unusual domain morphology. Individual domains of microscopic dimensions (as well as their extended networks) exhibit a peculiar bowl-like topology as determined through atomic force microscopy.



The presence of tall rims surrounding individual domains is consistent with the accumulation of squalene at the domain periphery, as well as a shift in isoprene chain orientation away from the substrate. Taken together, this evidence supports the notion that squalene has a role analogous to cholesterol in eukaryotic membranes, and that it might play a crucial role modulating chain order, lipid packing, and domain formation in the membranes of archaea.

COLL 645

Making magic with model membranes: Solution effects on solid support lipid bilayers

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Lipids are an integral part of life on earth, and while our knowledge of these compounds continues to increase, there is still much to be discovered in terms of lipid mechanics. Unfortunately these systems are far too complex to examine without interference, yet too small to observe effectively. Surface chemistry offers a well characterized system in which minute interactions can be observed on a sensor and recorded in real time. Using a combination of Quartz Crystal Microbalance (QCM) and Dual Polarization Interferometry (DPI) we were able to characterize the layer of hydration between a Solid Support Lipid Bilayer (SSLB) and the sensor surface, making it possible to calculate the effect of the solution on the electrostatic interactions in our system. Our research explores the effects of acidity and salinity on the layer of hydration and how this knowledge can be applied to further the SSLB model of cell membranes.

COLL 646

Directed organization of gold nanoparticles in polymer coatings over large length scales through infrared-assisted evaporative lithography

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There are various strategies to assemble nanoparticles (NP) over short length scales, but the organised arrangement of NPs over a large area to modulate optical and electrical properties is still remaining a challenge. We have recently developed a new, fast one-step route to create a polymer coating with periodic topographic patterns repeating with characteristic lengths on the order of a millimetre. In this presentation, we will report how we have added Au NPs to an aqueous colloidal dispersion and transported them to targeted positions during the formation of a patterned coating. In this method, which is called infrared radiation-assisted evaporative lithography, a lateral flow of both polymer and Au NPs in an aqueous dispersion is created by differences in the evaporation rate across the wet film surface. A directed transport of the Au NPs in the horizontal direction is possible by this technique. Ring or flake-like assemblies of the AuNPs embedded within the polymer in periodic dome-like structures are created, and the arrangement is tuned through variation of the sizes of the polymer particles and the Au NPs. The extinction coefficient (μ in units of mm^{-1}) was determined by transmission spectroscopy as a function of the lateral position with a step size of 50 μm . Depending on the process parameters, μ can be modulated between values of 3 and 14 mm^{-1} . Patterns prepared with smaller polymer particles lead to a stronger modulation of μ in the visible range, whereas stronger modulation in the IR-range was observed when larger polymer particles were used. The fundamental insights into controlling particle transport, which were acquired in this research, have applications in the creation of materials for SERS substrates and for coating photovoltaics.

COLL 647

Modulating the chemical, optical and transport Properties of isolated and self-assembled metal nanocrystals in 3D superlattices by changing their nanocrystallinity

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In this report, we will show that the crystallinity of nanoparticles can be controlled. It is well known that by submitted nanocrystals to laser beam, quadrupolar and breathing modes are observed. Here it is demonstrated for Au and Ag nanoparticles that the quadrupolar modes are splitted due to elastic anisotropy lifting of degeneracy mode whereas for Co nanoparticles, no changes in the breathing mode are observed.

Variations in the chemical properties of the nanocrystals of different structures, self assembled in compact hexagonal network are also observed.

We propose two mechanisms of fcc Au supracrystal (assembly of Au nanocrystals) growth. The solvent in which the Au nanocrystals are dispersed and their sizes are major parameters that determine the final morphology of nanocrystal assemblies in either films by layer-by-layer growth (heterogeneous growth), characterized by their plastic deformation, or well-defined shapes grown in solution (homogeneous growth). Specific properties related to the nanocrystallinity of supracrystals composed by nanocrystals are presented. Furthermore, low temperature electron transport properties measured by STM will be discussed.

COLL 648

Unraveling the evolution and nature of the plasmons in (Au core)/(Ag shell) nanorods

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Understanding the nature of the plasmon modes in noble metal nanostructures is of vital importance because different plasmon modes exhibit distinct optical properties, which in turn determine their plasmon-based applications. We have systematically studied the evolution and nature of the different plasmon modes in (Au core)/(Ag shell) nanorods. The plasmonic properties of the nanorods are essentially determined by the Ag shell and are tunable by synthetically changing the core size and shell thickness. With increasing shell thicknesses, four plasmon bands are observed. They are ascribed to the longitudinal dipolar mode, transverse dipolar mode, and two octupolar modes, respectively, in the order of decreasing plasmon wavelengths. The plasmon wavelengths and intensities of the four modes vary gradually versus the shell thickness. The retardation effect and the interference between the excitations are crucial for

exciting the two octupolar modes. Our results are useful for designing (Au core)/(Ag shell) nanostructures and utilizing their attractive and rich plasmonic properties for various plasmonic applications.

COLL 649

Plasmonic sensing materials for extreme temperature, harsh environment applications

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The ability to monitor gas species selectively, sensitively, and reliably in extreme temperatures and harsh conditions is critically important for more efficient energy production using conventional fossil energy based production technologies and enabling advanced technologies for fossil based power plants of the future. Optical based sensing platforms have become increasingly important but a need exists for materials that exhibit useful changes in optical properties in response to changing gas atmospheres in high temperature conditions. We will discuss recent experimental results on nanostructured or nanocomposite based thin films for plasmonic sensing at elevated temperatures and will discuss changes in optical properties in response to various high temperature gas treatments in the context of simple models for optical absorption in plasmonic materials.

COLL 650

High-Yield Single Product Synthesis of Ag₄₄(p-MBA)₃₀M₄ Nanoclusters

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Stellacci et al. reported synthesizing aryl thiol protected Ag₄₄(SR)₃₀ nanoclusters that were apparently single sized.¹ The optical spectrum had 8 distinct molecule-like absorption bands spanning the visible spectrum, giving rise to the term intensely and broadly absorbing nanoclusters (IBAN's)^{1,2,3}. These spectral properties make IBAN's good candidates for light-harvesting applications². Thus far, however, synthetic procedures have been time-consuming and produce low yields of relatively unstable clusters. For example, while solution phase stability is good, solid phase stability is poor, which restricts possible applications. In the present study, we directly synthesized pure Ag₄₄(p-MBA)₃₀M₄ clusters without size separations, as confirmed by mass spectroscopy, where p-MBA is p-mercaptobenzoic acid and M⁺ is a counterion. Yields >90% were achieved by judicious choice of reaction conditions and by stabilization of

the final product. These silver clusters were found to be stable in both solution and solid form for extended periods of time.

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COLL 651

Luminescent Noble Metal Nanoparticles

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Luminescent noble metal nanoparticles have emerged as a new class of fluorophores due to their unique photophysical properties and great potential in energy conversion, sensing and imaging. After a decade's effort, a large number of luminescent metal nanoparticles with different sizes and surface chemistries have been developed. While the luminescence is often attributed to size effect, other structural parameters such as surface ligands, valence states of metal atoms and crystallinity of nanoparticles also have significant influence on emission properties and mechanisms. In this talk, I will present some general strategies used to create luminescent gold nanoparticles with size from few atoms to tens of nanometers and discuss how these structural factors influence their photoluminescence properties.

COLL 652

Near IR Luminescence of Au Nanoclusters Tailored by Core-Ligand Interfacial Bonding

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Sub-2-nm Au thiolate nanoclusters are known to display strong near IR luminescence. The quantum yield of these nanoclusters depends on the chemical composition of $(Au)_x(Ligand)_y$, as well the charge states of the Au core and the ligand polarity. The emission has been attributed to the surface states established by Au-S bonding.

Inspired by the RS-Au-SR 'staple' thiol bridging motif discovered at Au nanoclusters passivated by monothiolate ligands, our group has recently employed a multidentate dithiolate approach to tailor the structure and energetics of the Au nanoclusters. The talk will discuss the means to further enhance the quantum yield of their near IR emission for bioimaging applications. Intensity and lifetime images of cancer cells loaded with these Au nanoclusters will also be discussed.

COLL 653

Synthesis of Concentrated Ag Colloids in Dodecane

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Synthesis of nanometer-sized Ag particles dispersed in hydrocarbons is of current interest due to potential applications of the colloids as agents for efficient heat transfer. Earlier studies showed that only dilute Ag colloids were accessible via photochemical reactions. Presented here is a simple technique that can yield stable Ag colloids with concentrations as high as 0.08 M, 1% by weight. Ag nanoparticles were achieved by thermal reduction of Ag(I) ions in dodecane, which acted as solvent and also as a reducing agent, whereas oleoyl sarcosine served as a particle stabilizer. The colloids were characterized by UV-Vis spectroscopy, optical microscopy, X-Ray diffraction, and transmission electron microscopy. The particles consist of fcc silver and are nearly spherical in shape with an average diameter of 6.4 nm. Optical microscopy has shown that 450 nm particle aggregates coexist with the nanometer-sized Ag particles in solution.

COLL 654

Shape-controlled synthesis of silver nanocrystals and their optical properties

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This presentation will center on our recent developments in shape-controlled synthesis of silver nanocrystals. The syntheses were based on the strategy of seed-mediated growth. The key to the success in shaping silver nanocrystals relied on our ability to control the growth of a seed along specific directions by using thermodynamic or kinetic approaches. Taking the overgrowth of silver cubic seed as an example, when the growth was controlled along the directions, truncated cubes, cuboctahedrons, and octahedrons were obtained. However, concave cubes, octapods, and trisoctahedrons were formed when the overgrowth was switched to the directions. The strategy was also successfully extended to other types of seeds (e.g., spherical and plate-like seeds),

producing a set of Ag nanocrystals with new shapes. Shape-dependent optical properties of those Ag nanocrystals will also be systematically discussed.

COLL 655

Soft microorigami: shape-programmed folding of stimuli-responsive polymer films

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Self-folding stimuli-responsive polymer films are exemplary biomimetic materials and can be viewed as model systems for bioinspired actuation. In this contribution, we demonstrate that the external shape of isotropic polymer bilayers is able to direct folding in a sophisticated manner leading to highly complex hierarchical folding. In particular, films can undergo sequential steps of folding by forming various 3D shapes with sharp hinges. By analyzing the folding patterns we elucidated empirical rules cross-checked by analytical considerations and backed up with finite-element simulations, which allow programming of folding and the design of specific 3D shapes such as pyramids. We also highlight the importance of path-dependency in the activation of the actuator, which enables to lock it in a local energy minimum, which can differ from the global one.

COLL 656

Light-triggered hydrophobicity switch to control assemblies of azobenzene-containing copolymers with micelles, lipid and cell membranes

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We tailored azobenzene-modified poly(acrylic) acids to optimize the remote control by exposure to light of hydrophobic (self-)assemblies in aqueous media. Experimental illustrations include photo-switch of their mixed micellization with surfactants⁽¹⁾, and light-triggered permeabilization of lipid vesicles and plasma membrane of mammal cells⁽²⁾. To analyze the measured fractions of bound hydrophobes (here azobenzene) as a function of the density of hydrophobic groups per chain, we propose a model based solely on one parameter: The critical hydrophobicity of a (bound) polymer segment.⁽¹⁾ This model enables us to discuss a bottom up approach for the design of optimal responses to light and it predicts non-monotonic variation of LCST that were recently evidenced.⁽³⁾

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COLL 657

Responsive Microcapsule Dimers Assembled in-situ by a Microfluidic Technique

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We describe the creation of soft microscale assemblies that can propel themselves in the presence of a chemical fuel or can be actuated by an external magnetic field. These assemblies are created in situ within a microfluidic platform using the biopolymer chitosan as precursor. Our approach generates individual microscale droplets bearing chitosan, which are then made to undergo controlled cross-linking and coalescence into higher-order structures such as dimers or trimers. The size, shape, and functionality of each individual capsule within the dimer or trimer can be precisely controlled. For example, we have prepared dimers wherein one lobe contains nanoparticles of platinum (Pt). Such capsule dimers undergo self-propelled motion in water upon the introduction of hydrogen peroxide (H_2O_2) to the solution. In this case, the catalytic reaction of H_2O_2 with the encapsulated Pt produces oxygen gas, and the expulsion of this gas from the capsule in the form of bubbles propels the dimer forward in a direction away from the Pt-containing lobe. Similarly, magnetically responsive dimers can be created by substituting the Pt with paramagnetic Fe_2O_3 nanoparticles. The resulting dimers undergo controlled rotation in an external magnetic field, much like a magnetic stir bar. The overall approach described here is simple and versatile: it can be easily adapted in a multitude of ways to produce soft structures with designed functions and properties.

COLL 658

Core-shell superparamagnetic nanoparticle membranes

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Nanoparticles with ultrastable and carefully controlled core-shell structures can be used in biomedical applications, e.g., as biomedical imaging contrast agents or in hyperthermia. Exquisite control allows further applications through assembly into biomimetic membrane and vesicular structures for which permeability can be externally controlled by applied magnetic fields.

I will describe a synthetic toolkit built on nitrocatechol dispersants and the synthesis of monodisperse Fe_3O_4 cores to investigate membrane assembly of superparamagnetic nanoparticles at liquid interfaces and into lipid membranes. The relationship between nanoparticle structure and the assembled membrane structure and actuation will be highlighted using combinations of techniques ranging from SANS to FreSCa developed to measure the surface energy of single nanoparticles down to 10 nm in diameter. I will demonstrate that the extension and stability of the nanoparticle shell structure determines the energetics of nanoparticles at oil-water interfaces and in lipid membranes.

COLL 659

Reversible light-controlled compaction of soft colloids by azobenzene containing surfactant

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Nature has found very clever mechanism how to store a very long DNA molecule in a very small and compact region of space. The scientific interest in the DNA compaction is two folds: on the one hand, it is challenging to understand how nature does this trick, on the other hand, one would like to imitate this process for certain reasons, the most prominent of which is gene delivery into cells. In our study inspired by the DNA compaction mechanisms we are using light as external optical stimuli in order to trigger the swelling behavior of two system: DNA macromolecule and microgels. In order to achieve reversible compaction/decompaction process we have employed a cationic photosensitive azobenzene-containing surfactant. UV-light irradiation results in trans-cis isomerization of the azobenzene unit incorporated into the surfactant-tail and causes an unbinding of the more hydrophilic cis-isomer from the negatively charged soft colloid and its reversible swelling.

COLL 660

Tunable release of metal ions from polyelectrolyte-ion complex film

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The Layer-by-Layer (LbL) technique has been given a great attention due to the ease with which thin films based on the complexation of oppositely charged polyelectrolytes can be fabricated. Due to the charged nature of polyelectrolytes which may or may not have condensed counterions, the interaction of these functional groups with small ions, especially metal ions, are extremely complex. Multivalent metal ions can act as crosslinkers to enable the construction of ligand polymer with them for sensing

capabilities or developing ion-ligand polymer for tunable release of biological molecules by chelation. Ionic crosslinks formed through polycations, polyanions and multivalent ions can be reformed or reconstructed with time. Here, we choose metal ions as the small ionic crosslinker and weak polyelectrolytes, branched polyethyleneimine (BPEI) and polyacrylic acid (PAA), to build the polyelectrolyte-ion complex film. The release of these metal ions can be controlled by factors such as pH, salt and other ligands.

COLL 661

Reversible absorption of protons by temperature-responsive gel-particles

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Synthetic materials that reversibly absorb target molecules in response to external stimuli are of great interest. Recently, it has been reported that gel-particles (GPs) consisting of *N*-isopropylacrylamide (NIPAm) and functional monomers reversibly absorb target molecules such as protein, peptide and CO₂ via a phase transition induced by temperature change. In this study, we report that GPs with reversible affinity to proton can be prepared by copolymerizing acrylic acid (AAc) in the presence of a high concentration of proton. In the proton-rich condition, AAc were fully protonated and thus efficiently incorporated into low polarity domain of growing PNIPAm GPs. As a result, strong proton binding sites were constructed in the GPs. By cooling below phase transition temperature, PNIPAm were hydrated and carboxylic acids in PNIPAm were exposed into water, resulting in effective release of proton. Importantly, strong proton binding sites were regenerated reversibly by heating above phase transition temperature.

COLL 662

Responsive carbon nanotube supraparticle assemblies for water purification

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We have chemically functionalized single and multi-walled carbon nanotubes and covalently attached small magnetic beads to them. Bead-tube assembly is responsive to small magnetic fields. The assemblies can be completely removed from dispersion by magnetic actuation and then re-dispersed with mixing or mild sonication. Our goal is optimize the specific surface area and hydrophilicity of supraparticle assemblies that are capable of removing dissolved organic content from aqueous media. Details of the synthesis and control over the bead:tube ratio, light scattering and microscopy of the

assemblies, magnetic and dielectric responsivity, and solute adsorption characteristics will be presented.

COLL 663

Reversible absorption of CO₂ by aqueous solution of amine-containing poly-*N*-isopropylacrylamide particles

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It has been reported that hydrogels consisting of *N*-isopropylacrylamide (NIPAm) and functional monomers reversibly capture target molecules such as dyes, drugs, peptide, proteins via temperature-responsive volume phase transition. In this study, we report that aqueous solutions of micro- and nanogel particles (GPs) consisting of NIPAm and amine-containing monomers reversibly absorbs and desorbs CO₂ via the phase transition induced by cooling and heating cycles. Below the phase transition temperature, most amines in the GPs are capable of forming ion pairs with bicarbonate ions. Above the phase-transition temperature, shrinkage of the GPs lowers the pKa of amines, resulting in almost complete desorption of CO₂.

COLL 664

Bespoke patterned coatings via infrared radiation-assisted evaporative lithography: Moving colloids with modulated light

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Polymer coatings with periodic topographic patterns, repeating over millimetre length scales, are created from lateral flows in an aqueous dispersion of colloidal particles. The flow is driven by differences in evaporation rate across the wet film surface created by IR radiative heating through a shadow mask. Thus, in this new process, which we call IR radiation-assisted evaporative lithography (IRAEL), particle transport is controlled through IR light acting at a distance through mask. We show that the height of the surface features increases with an increase in several key parameters: the thickness of the colloidal film, the volume fraction of particles, and the pitch of the pattern. The results are interpreted by using models of geometry and particle transport. The patterned coatings can function as “paintable” microlens arrays, applicable to nearly any surface, and able to focus light at short focal lengths. Compared with existing methods for creating textured coatings, IRAEL is simpler, inexpensive, able to create a wide variety of bespoke surfaces, and applicable to nearly any substrate without prior preparation.

COLL 665

Effects of block copolymer properties on nanocarrier protection from in vivo clearance and targeting

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Drug nanocarrier clearance by the immune system must be mitigated in order to achieve targeted delivery to pathological tissues. We present two parts to the problem: first, the relationship between nanoparticle block copolymer chemistry and passivation against non-specific recognition and clearance; and second, how conjugation to the surface of the nanoparticle can effect targeting. We have produced hydrophobic nanocarriers with dense PEG layers resulting from block-copolymer-directed assembly during rapid precipitation. Nanocarriers were formed using block copolymers with hydrophobic anchor blocks of polystyrene (PS), poly- ϵ -caprolactone (PCL), poly-D,L-lactide (PLA), or poly-lactide-co-glycolide (PLGA), and hydrophilic blocks of polyethylene glycol (PEG) with various molecular weights, from 1.5 kg/mol to 9 kg/mol. Nanocarriers with paclitaxel prodrugs were evaluated *in vivo* in Foxn1 nu mice to determine relative rates of clearance, and *in vitro* complement activation assays were conducted in an effort to correlate the protection of the nanocarrier surface with *in vivo* circulation. Guidelines for optimizing block copolymer structure to maximize circulation of nanocarriers formed were proposed, relating to the relative size of the hydrophilic and hydrophobic block, the hydrophobicity of the anchoring block, the absolute size of the PEG block, and secondary consideration such as polymer crystallization. The second aspect of the presentation is on targeting. A fraction of PEG chains on the nanoparticle surface can be conjugated with targeting ligands, including small molecules (mannose to target to TB infected macrophages), peptide sequences (LHRH for breast cancer), and full antibodies (anti-EGFR mAb C225). The reactivity of different size ligands onto the PEG brush layer poses interesting challenges to understanding reactions in constrained media. Furthermore, the targeting efficiency is shown to not be a simple function of the density of the ligand on the nanoparticle surface. This opens interesting questions about the role of ligand and receptor density on binding and uptake.

COLL 666

Synthesis and Characterization of Drug-Polysaccharide Nanoparticles for Oral Drug Delivery Applications

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Nanoparticles comprised of drugs encapsulated in carboxymethyl cellulose acetate butyrate (CMCAB) were produced by rapid precipitation and the formulation process and properties of the nanoparticles were investigated. The purpose of this research was two-fold. First, the methodology for producing drug-polymer nanoparticles with well-defined particle size distributions was developed. Second, the factors affecting drug loading and release properties were investigated. An antibacterial drug and a less soluble anti-viral drug were selected as model drugs for this study. The nanoparticles were formed under turbulent conditions in a multi-inlet vortex mixer. Particle diameters ranged between 150-400 nm with narrow polydispersity indices as measured by dynamic light scattering. The antibiotic drug loading efficiencies ranged from 14-40% whereas, for the less soluble antiviral drug, drug loading efficiencies were as high as 85%. Dissolution studies showed an increase in the solubility of the amorphous drug nanoparticles due to interactions with CMCAB.

COLL 667

Multicomponent PRINT hydrogel particles as a delivery platform for vaccines

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Current immunology research has focused on controlled delivery of antigens and adjuvants in order to safely build protection against pathogens. These components have shown increased efficacy when delivered in particulate form compared to soluble administration. Herein, we use PRINT[®] (Particle Replication In Non-wetting Templates) to fabricate polymeric hydrogel nanoparticles for the delivery of novel pro-adjuvants and protein antigens *in vitro* and *in vivo*. Silyl ether based pro-adjuvants show tunable release of active adjuvant when exposed to the acidic pH of the endosome while avoiding systemic release at physiological pH. Additionally, pro-adjuvants are functionalized with an acrylate group, allowing for direct polymerization into the particle matrix and precise control over cargo loading. Protein antigens are conjugated to the surface of nanoparticles through PEG linker chemistry for antigen processing and presentation by immune cells. Therefore, adjuvants and antigens can be loaded into the same nanoparticle for controlled delivery of therapeutically relevant components.

COLL 668

Therapeutic efficacy and pharmacokinetics of long-circulating PRINT hydrogels containing Cisplatin

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Circulation persistence has been established as a key characteristic of nanoparticles for passively targeting tumors, an important facet of chemotherapeutic delivery. However, many drugs are hindered by toxicity issues. Notably, Cisplatin—approved for use in a wide variety of cancers—has significant renal and neurological toxicities. Incorporating the drug into a nanoparticle increases tumor accumulation while simultaneously reducing side effects caused by systemic exposure.

We have formulated and optimized PEGylated, polymeric hydrogels using the PRINT platform, and complexed Cisplatin into the particles. The maximum tolerated dose of the particles is being determined and compared to free drug. Cytotoxicity in several lung carcinoma lines is being investigated, and efficacy studies in mice will be carried out in both subcutaneous and orthotopic non-small cell lung xenografts (A549). Renal toxicity and neuropathy will also be assayed. We anticipate reduced side effects and higher survival probability compared to the current standard of care.

COLL 669

Magnetic quantum dot enabled technologies for nanoscale manipulation

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The development of atomic force microscopy, magnetic tweezers, and optical tweezers has greatly enhanced our ability to manipulate matter at the nanoscale. However, these technologies have significant limitations, for example the challenge of manipulating

multiple objects in parallel or simultaneously tracking and manipulating objects with nanometer scale precision. Here, we describe a technology platform termed M³ technology, which combines magnetic quantum dots, micropatterned magnetic field engineering, and molecular motor-based control, to overcome these limitations. Some of its key capabilities will be presented here, including: (1) manipulation and tracking of multiple individual nanoparticles and cells (leucocytes), (2) multiplexed sub-femtomolar detection *and* isolation of protein and/or DNA molecules, and (3) steering, capture, and shape manipulation of self-assembled structures already in motion. This highly versatile technology platform will lead to numerous new opportunities in nanotechnology, chemistry, and bioengineering.

COLL 670

The atomic metron - a basis for synthesis of sub-nanometer particles with known sizes and a discrete number of atoms

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Sub-nanometer nanoparticles (NPs) are very intriguing for the scientific community due to numerous characteristics they possess. Size control and homogeneity of metal NPs during synthesis and characterization are extremely important parameters to consider. A general method is proposed to generate nanoparticles with a defined number of atoms in the metal core by incorporating “atomic metrons” as the macromolecules with defined number of binding sites as the matrix. Synthesis, characterization, and purification of the atomic metrons with known binding sites will be discussed. Furthermore, filling all the binding sites with metal atoms and transformation to NPs will be demonstrated.

COLL 671

Modular fluorescent poly(organosiloxane) nanoparticles for biomedical applications

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We report the synthesis and characterization of multifunctional and fluorophore-labeled, charge- or sterically stabilized poly(organosiloxane) core-shell nanoparticles with tunable surface properties.

The core-shell approach allows independent functionalization of different compartments. Thus, the fluorophore was efficiently incorporated into the core during polycondensation. Electrostatic stabilization of nanoparticles was achieved subsequently by introduction of functional groups on the surface. Grafting of polymers (e.g. thermo-responsive poly(2-isopropyl-2-oxazoline)) leads to sterically stabilized biocompatible nanoparticles.

The particles were characterized by multi-angle Dynamic Light Scattering (DLS), Asymmetrical Flow Field-Flow Fractionation (AF-FFF) and Zeta-potential measurements and additionally by electron microscopy (TEM, Cryo-TEM). The spectroscopic properties were studied by fluorescence spectroscopy including the determination of absolute fluorescence quantum yields.

Due to their modular structure and ease of functionalization, poly(organosiloxane) systems are suitable for various biomedical applications e.g. imaging methods, specific targeting and drug delivery. In this context, cell experiments are performed and nanoparticles are applied to lung-tissue models.

COLL 672

Facile synthesis of ultrasound responsive hollow silica particles with ultrathin nanometer-scale shell structures

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Hollow nanomaterials have attracted intense attention because of their wide range of applications in imaging, chemical sensing, encapsulation, energy storage, catalysis and controlled drug release. The research of hollow particles are emphasizing on design of complex structures including double shelled, rattle like and yolk shell structures in recent years, but the synthesis of ultrathin hollow particles which can be cracked by ultrasonic treatment is seldom reported. In the present study, we report a novel preparation method for hollow particles where an ultrathin silica shell is formed extremely rapidly along the gas-liquid interface of an aerosol droplet. With decreasing silica precursor (TEOS) loading, the thicknesses of silica shell decreases (the lowest limit is approximately 10 nm) due to less silicate condensation reaction. These ultrathin hollow silica particles can be conveniently ruptured using ultrasonic cavitation effects. The porosity of the silica shell can be also adjusted by introducing sodium chloride into

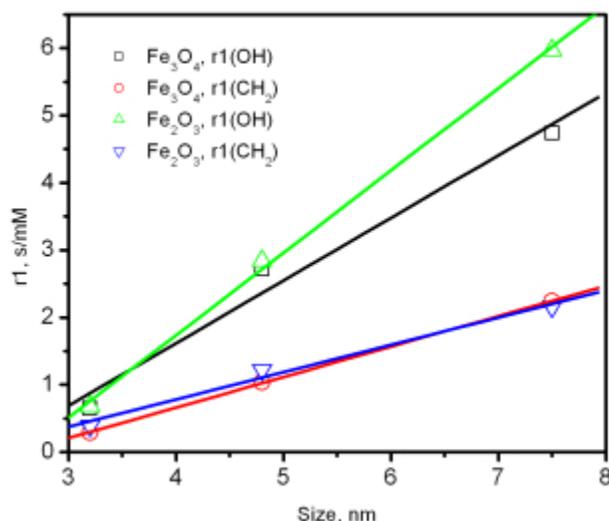
the precursor solution and the incorporation of magnetic iron oxide into the hollow silica particles provides further opportunities in magnetic stimuli responsive applications.

COLL 673

Superparamagnetic iron oxide nanoparticles with variable size and iron oxidation state as prospective imaging agents

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Colloidal magnetite nanoparticles were synthesized by high temperature hydrolysis of the precursor iron(II) and iron(III) alkoxides in diethylene glycol solution. The average particle sizes 3.2-7.5 nm were adjusted by changing the reaction temperature, time, and by using sequential growth technique. To obtain maghemite particles in the same range of sizes, magnetite particles were oxidized with oxygen in diethylene glycol at room temperature. The products were characterized by DLS, TEM, X-Ray powder diffractometry, TGA, FTIR and magnetic measurements. NMR r_1 and r_2 relaxivity measurements in water and diethylene glycol (for OH and CH₂-protons) have shown the decrease in r_2/r_1 ratio with the particle size reduction, which correlate with magnetization values for magnetite nanoparticles.



It was also found that saturation magnetization of magnetite is 20% higher than for maghemite, but their relaxivity properties are similar. This might be beneficial for application of maghemite as an imaging agent.

COLL 674

Fluorescence Active Laser Induced Structures

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High sensitive fluorometric techniques have made fluorescence a powerful tool in the study of structures and dynamics of living and non-living systems. The fluorescent properties changes with change in the microenvironment of the emitting molecule and this provides the ability to get spatial and temporal information of the system. The changes in the microenvironment can be physical and chemical such as temperature, pressure, viscosity, pH, hydrogen bonding, polarity, ions, electrical potential, and quenchers. Some of the common fluorescent probes suffer from photo bleaching, quenching and low fluorescence quantum yield. These problems can be easily overcome by Ag metal particles based fluorescent probe or structures.

The work we are reporting here describes the formation of structures on Ag nanoparticles based film using a laser. These Laser-Induced Structures (LIS) are 7 to 30 microns wide and highly fluorescent active. The advantages of Ag nanoparticles are surface enhanced Raman scattering, tunable surface Plasmon resonance (SPR) peak wavelength, metal enhanced fluorescence (MEF), and enhanced thermal and conductivity applications. These LIS have potential in the field of anti-counterfeiting, marketing techniques, fluorescent probes, bar-coding applications, optical grating, 3-D holographic structure making, micro fluidic devices and soft lithographic techniques. These structures are also easy to handle (only optical microscope required), simple and inexpensive to make.

COLL 675

Characterization of the secondary structure of surface-bound peptides

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In the research described here, we chemically functionalize gold surfaces with peptides of known secondary structure. These surfaces are chemically characterized through X-ray photoelectron spectroscopy, ellipsometry, and surface infrared spectroscopy. Furthermore, we use surface infrared and circular dichroic spectroscopies to characterize the structure and orientation of the peptide on the surface. We demonstrate that correctly functionalized surfaces induce an alpha-helical secondary structure on a peptide that is disordered in solution. Demonstration of the control over a desired secondary structure of helical elements at a chemically functionalized surface is an important advance in preparing robust biologically mimetic surfaces and is expected

to lead to an entirely new mechanism through which biological and inorganic materials can be coaxed to interact.

COLL 676

Orthogonal Immobilization Strategies based on Chemical Vapor Deposition Polymerization

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The detailed control of surfaces that present multiple biological cues in form of peptides, proteins, sugars or DNA is a critical requirement for a number of different applications. In particular, such strategies require the incorporation of multiple, orthogonal chemical groups within the same surface. Spatial localization of different groups as well as gradient designs are other important design features. There is thus a need for generally applicable, substrate independent surface modification strategies that provide orthogonal immobilization. Herein, I will discuss recent progress in my group with orthogonal biointerfaces that take advantage of chemical vapor deposition polymerization. Examples with orthogonal surfaces including those that can undergo "double-click" reactions will be discussed and a number of potential biomedical applications will be outlined.

COLL 677

Plasma-surface modification for improved biocompatibility and next generation biomaterials

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Three dimensional (3D) substrates have become of interest because of their potential uses in a range of applications, including tissue engineering. Plasma surface modification of biodegradable polymers such as poly (ϵ -caprolactone) (PCL) have been studied, with a focus on depositing thin films onto 3D polymer scaffolds. We used inductively-coupled plasmas to explore plasma surface modification of porous 3D PCL scaffolds with non-depositing systems such as H₂O, N₂, and Ar, creating permanently hydrophilic surfaces, some with high N content. Preliminary results from cell-seeding studies suggest Soas-2 osteoblast cells have a higher affinity for modified scaffolds than untreated substrates, and substrates with high N incorporation show additional increases in cell growth within scaffolds. This presentation will focus on challenges associated with both surface modification strategies for 3D substrates and challenges

associated with appropriate and accurate characterization of these materials. Additional results from alternate scaffold materials and plasma chemistries will be presented.

COLL 678

Plasma processes for life sciences

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Cold plasmas are extensively utilized to modify materials surface in a growing number of applications, from microelectronics, to food packaging and biomedical materials. Plasma processes at low and atmospheric pressure impact three large areas of medicine and biology, namely, surface modification of devices for eliciting the best response of biofluids and tissues in contact with the modified material; sterilization/decontamination of biomedical materials; and plasma medicine, the direct exposure of living tissues to plasmas (e.g. for wound sterilization and healing, blood clotting, cancer treatments, surgery, etc.). Plasma medicine is a newly developed field focused on understanding how to modulate effects such as cell activation, apoptosis and necrosis as a function of the "dose" of plasma (density of active species, radiations, charges) delivered. This talk focuses on recent advances on deposition and grafting plasma-processes for tissue engineering and regenerative medicine, aimed to properly tailor the surface of materials for biomedical applications.

COLL 679

Sensing a deadly touch- Methods for evaluating contact-active antibacterial materials

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Contact-active antibacterial materials are a type of biomaterial that inactivates bacteria upon physical interaction. No toxic pollutants are released, thus both the risk of emergence of bacterial resistance is reduced and the active life-span of the material is prolonged compared to common antibacterial materials that are leaching. The testing of such materials is not straightforward as established microbial techniques are developed for the leaching mechanism. However, as the contact-active surfaces have gained increasing interest, so have the need for proper evaluation tools. This talk will cover the existing methods and benefits and limitations of them. Especially a method developed by us to detect the contact-activity of a cellulosic fibre material will be presented.

Cellulosic fibres are interesting for future materials as they are both renewable and easy to modify in order to obtain the desired properties but the nature of the fibres do also introduce additional difficulties.

COLL 680

Understanding molecular-scale separations on agarose supported peptide surfaces

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Acquiring a molecular-scale understanding of adsorptive separations is important because of the current high cost of purification associated with the manufacture of biologically-based pharmaceuticals. Single-molecule fluorescence microscopic methods were developed to study the dynamics of the protein α -lactalbumin at a clustered-charge anion-exchange chromatographic adsorbent interface with an unprecedented level of detail. Dissociation and association kinetics and corresponding equilibrium constants were calculated for single and clustered adsorbents, and binding events were mapped using super-resolution techniques at ~ 40 nm length scales. Additional spectroscopic advancements required for these studies include the derivation of Maximum Likelihood Estimation (MLE) methods for optimizing the analysis of single-molecule trajectories that accommodate phenomena such as experimental noise, photoblinking, photobleaching, and translation or rotation out of the collection plane.

COLL 681

Tailoring the surface of inorganic nanoparticles: polymer coating

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Colloidal stability of nanoparticles (NPs) in aqueous media is a key issue. Current colloidal chemistry methods for the synthesis of inorganic nanoparticles can produce NPs either soluble in polar or non-polar solvents which typically have to be derivatized into colloiddally stable materials. There are a number of strategies to derive water “soluble” inorganic nanocrystals including ligand exchange with small, macro or bio-molecules, polymerization of a silica shell, wrapping in organic polymers, encapsulation, or combinations of the aforementioned.¹⁻³ Coating of NPs with amphiphilic polymers provides a universal derivatization route for inorganic NPs of distinct compositions, sizes and shapes, enabling tailoring for specific purposes.⁴ Polymer coating of a number of model NPs will be discussed.

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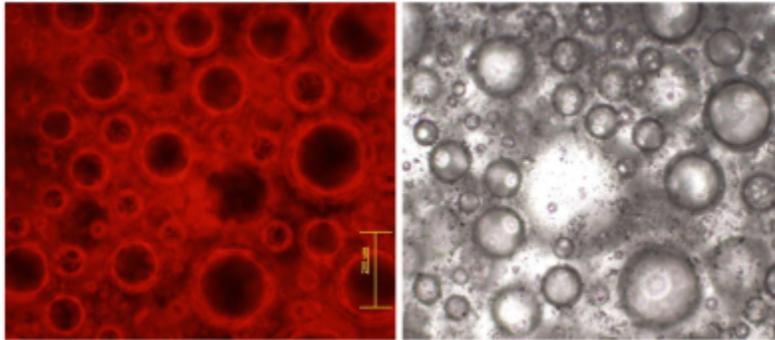
COLL 682

Functional responsive foams stabilized with particles of engineered shape and structure

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We will discuss how particles with anisotropic shape and engineered properties can be synthesized and applied in the formation of Pickering foams and emulsions with novel functionality. These particles are synthesized by "liquid nanofabrication" in biphasic liquids under shear. We demonstrated earlier the large-scale fabrication of polymer microrods and reported how they act as superstabilizers of foams and emulsions by forming rigid adsorption shells around the bubbles or droplets. The method allowed synthesizing HMC and lignin particles that can enrich Pickering foams and emulsions with additional features such as color, specific rheological response, stability against drying, controlled destabilization and controlled release. We will present means of making strongly and selectively colored foams by co-precipitating HMC with dye. We will also demonstrate how the inclusion of magnetic particles in the HMC matrix allows making "magneto-Pickering" foams, which exhibit excellent stability in the absence of a magnetic field, but can be destroyed quickly and on demand with the application of a threshold field. The rheological characteristics and collapse behavior of these foams can be correlated to the liquid fraction as well as the concentration of magnetic particles in the lamellae. The use of lignin particles as foam stabilizers allows making stable foams with gel-like films between the bubbles. These novel systems provide

fundamental insights on the properties of Pickering foams, and can find applications in processes requiring immediate non-contact defoaming.



COLL 683

Water-in-water emulsions for the design of hydrogel based drug carriers and biomaterials

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At elevated concentration, aqueous polymeric solutions exhibit phase separation. Here we demonstrate how this property can be explored to fabricate hydrogel drug carriers and biomaterials. A first example is based on phase separation of dextran and poly(ethyleneglycol) (PEG), by optimizing the system to obtain dextran droplets in a continuous PEG phase. Using dextran that is modified with either azide/alkyne “click” moieties of polymerizable methacrylate moieties (both connected to the dextran backbone via a hydrolysable carbonate ester), degradable hydrogel microspheres can be formed. Interestingly, due to preferential distribution of proteins in a dextran rather than in a PEG phase, these dextran microspheres can accommodate relatively high amounts of proteins. Furthermore, Layer-by-Layer coating of these hydrogels creates so-called self-exploding capsules that release their protein payload upon degradation of the carbonate ester cross-links and the resulting sudden increase in osmotic pressure. A second example is based on phase separation of gelatin and PEG. By optimizing the system to obtain a continuous gelatin phase, microporous gelatin scaffolds are obtained that allow further engineering with growth factor gradients that can affect cellular behavior.

COLL 684

Fabrication of Microgel-in-Liposome Particles for Improving Skin Barrier Functions

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Here we describe a method for fabricating a microgel-in-liposome (M-*i*-L) structure consisting of a microgel and a lipid shell in order to mimic corneocyte cell structures. The essence of our approach is to use a lecithin-based microemulsion with a very low interfacial tension between the oil and water continuous phases to stabilize a dispersion of microgel particles. To demonstrate the applicability of this unique vesicle system, we encapsulated a high concentration of natural moisturizing factor (NMF) in the microgel core and investigated how the M-*i*-L structure affected the water retention in comparison with other control systems. We have observed that our M-*i*-L particles with the NMF in the core, which mimicked the corneocyte cell structure, showed an excellent ability to retain water in the system. This experimental result inspired us to investigate how corneocyte cells, which feature a lipid-enveloped hydrogel structure, provide such long-lasting hydration to the skin.

COLL 685

Ultrastrong bubble-templated shells for lightweight materials

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Lightweight materials with high mechanical strength are extremely useful for a variety of applications in transportation, aerospace and military equipment. Hollow particles are often used to generate lightweight materials with high strength. We present a new method for fabricating monodisperse hollow shells with unique mechanical behavior. We demonstrate that nanoparticle-shelled bubbles, produced using microfluidics, can be reinforced with different heat treatments. The stiffness and the strength of the bubbles can be increased by several orders of magnitude. We characterize the mechanical properties and fracture mechanisms of bubble-templated shells at the single particle level using in-situ compression as well as ex-situ nanoindentation. Finite element analysis is used to verify the stress distribution within the shell during the mechanical tests. We show some examples of lightweight hybrid materials that incorporate these reinforced shelled-bubbles.

COLL 686

Lightweight and strong cellulose materials made from aqueous foams stabilized by Nano Fibrillated Cellulose (NFC)

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A novel, lightweight and strong porous cellulose material has been prepared by drying aqueous foams stabilized with surface modified NanoFibrillated Cellulose (NFC). Confocal microscopy and high speed video imaging shows that the long-term stability of the wet foams can be attributed to the octylamine-coated, rod-shaped NFC nanoparticles residing at the air-liquid interface preventing the air bubbles to collapse or coalesce. Careful removal of the water results in a porous cellulose-based material with a porosity of 98 % and a density of 30 mg cm⁻³. These porous cellulose materials have a higher Young's modulus than other cellulose materials made from freeze drying and a compressive energy absorption of 56 kJ m⁻³ at 80 % strain. The pore size distribution is measured with the aid of an autoporosimeter and reveals that most pores are in the range of 300 to 500 µm.

COLL 687

Soft Nanoemulsion Composites: Synthesis, Assembly and Applications

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Nanoemulsions are metastable dispersions containing nanoscale liquid droplets in another immiscible fluid. These dispersions find widespread use in biological, cosmetic, and pharmaceutical applications. Recently my group has been developing new methods to synthesize soft nanoemulsion composites with programmed material properties. First, I will discuss our recent discovery of mesoporous organohydrogels from oil-in-water nanoemulsions containing an end-functionalized oligomeric gelator in the aqueous phase. The nanoemulsions exhibit an abrupt thermoreversible transition from a low-viscosity liquid to a fractal-like colloidal gel of droplets with mesoscale porosity and solid-like viscoelasticity with moduli approaching 100 kPa, possibly the highest reported for an emulsion-based system. We hypothesize that gelation is brought about by temperature-induced interdroplet bridging of the gelator, as shown by its dependence on the gelator chemistry. Next, I will discuss leveraging the ability to create high volume fraction (>50%) optically transparent and photocrosslinkable nanoemulsion dispersions. Crosslinkable nanoemulsions are combined with flow lithography for the synthesis of structured composite microgels with controlled hydrophobic compartments. The microgels are used to demonstrate a number of motifs for controlled encapsulation and

release of active compounds, including small molecules, proteins, and nanoparticles, from a single material platform.

COLL 688

One step preparation of monodisperse complex emulsions by phase separation

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Emulsions with complex geometries, including multiple emulsions, Janus emulsions, or multilayered emulsions, have been interested because of their significant potential in many applications such as foods, pharmaceuticals, cosmetics, materials, and chemical separations. Here, we present a simple one-step approach for the generation of complex emulsions using phase separation of disperse droplet in a microchannel. The microfluidic system can figure out the basic principle of phase separation attributed from mass-transfer of separating agent triggering control of the formation of complex emulsions. Single step method mediates precision control of the size of droplets, efficient encapsulation as well as compartment of active ingredient into desired position in an emulsions droplet. The ability to generate morphologically complex emulsions and particles provides distinct advantages over shape and chemical anisotropy. Moreover, these orthogonal properties motivate us to develop a simultaneous encapsulation of hydrophobic and hydrophilic compounds into desired specific compartment.

COLL 689

Ethyl gallate-responsive monodisperse microspheres and microcapsules prepared with emulsions as templated templates

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Monodisperse poly(N-isopropylacrylamide) (PNIPAM) microspheres and microcapsules are prepared with emulsions as templates. and the responsive properties of prepared microspheres and microcapsules to ethyl gallate (EG) are investigated systematically. Monodisperse W/O and O/W/O emulsions are generated by capillary microfluidic devices, and monodisperse microspheres and microcapsules are prepared by polymerizing the water phases. The volume phase transition temperature (VPTT) of PNIPAM microspheres in aqueous solutions with varying EG concentrations is investigated and the change in size and structure of core-shell PNIPAM microcapsules in response to varying temperature and EG concentration is investigated visually by using a confocal laser scanning microscope (CLSM). From the experimental data, a

state diagram of the intact-to-broken transformation of core-shell PNIPAM microcapsules in aqueous solution as a function of temperature and EG concentration is constructed for the first time. The results in this study provide valuable information for the development of some simple and cheap techniques for roughly detecting the EG concentration by using core-shell PNIPAM microcapsules as sensors and/or indicators.

COLL 690

Stimuli-responsive polymeric microcapsules prepared by emulsion template methods

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Functional polymeric microcapsules have been widely used in both industrial and high-tech fields, including foods, fine chemicals, medicine, biochemistry and electronics. Combination of microfluidic emulsifications and traditional microencapsulation has been extensively studied for preparation of monodisperse microcapsules. In this study, 3D capillary microfluidic technique is used to produce uniform double emulsions, which serve as templates for synthesis of stimuli-responsive functional polymeric microcapsules. Using oil-in-water-in-oil (O/W/O) double emulsions as templates, the pH-responsive chitosan microcapsules and thermo-responsive poly(*N*-isopropylacrylamide) (PNIPAM) microcapsules are generated by interfacial crosslinking and free-radical polymerization, respectively. The chitosan microcapsules can decompose completely within 39 s when pH is as low as 1.5. Upon increasing the environmental temperature and alcoholic concentration, the PNIPAM microcapsules undergo the complete release of inner oil cores with a high momentum. The stimuli-responsive functional polymeric microcapsules show great potential in enzyme immobilization, controlled release and sensors and actuators.

COLL 691

Smart core-shell particles for enhanced oil recovery applications

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We use capillary microfluidics for precise formation of double emulsion templates to fabricate core-shell particles; for example, by polymerizing a droplet middle layer to form capsules with a consolidated membrane. We use this strategy to fabricate capsules with potential application in enhanced oil recovery. We create capsules with fluorinated crosslinked polymers using in-situ photopolymerization to create inert membranes with ultra-low permeability. We include acrylate linkages in the polymer matrix as degradable components; these acrylate linkages are oxidized to present a simple mechanism for timed release of actives. Additionally, we use microfluidics to fabricate oil-absorbing

core-shell particles with a hydrophobic porous core protected by a hydrophilic shell; the shell is made hydrophilic by silica nanoparticles adsorbed at the surface. These particles have great promise for use in oil remediation or EOR applications.

COLL 692

Theory of DNA-cationic micelle complexation

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We present a theory of spherical micelle formation from cationic amphiphiles in the absence and in the presence of DNA. The distribution of micelle sizes as well as the critical micelle and aggregation concentrations (cmc and cac) are calculated. Micelle formation is favored by the hydrophobic tails but disfavored by the entropic cost associated with counterion condensation. Counterion release drives the complexation between DNA and amphiphiles and causes micellation at a much smaller concentration than in the absence of DNA. The stiffness of double-stranded DNA favors the formation of large micelles leading to a bimodal distribution of micelle sizes.

COLL 693

Characterization of the nanostructure of complexes formed by single- or double-stranded oligonucleotides with cationic surfactants

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This presentation will describe the use of dynamic light scattering (DLS), small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS) measurements to compare and contrast the nanostructure of complexes formed by single- or double-strand oligonucleotides with the single-tailed cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), in aqueous solutions. Whereas SAXS and SANS spectra show that single-strand oligonucleotides and CTAB form multilamellar vesicles, double strand oligonucleotides and CTAB form a hexagonal nanostructure. In addition, our results reveal that the nucleotide composition of the single-strand oligonucleotides has a pronounced impact on the number, size and nanostructure of the complexes formed with CTAB. In contrast, for double-strand oligonucleotides, no evidence of a composition dependence on nanostructure was measured. These results support the proposition that hydrophobic interactions, as well as electrostatics, play a central role in the formation of complexes between cationic amphiphiles and single-strand oligonucleotides and thus giving rise to interactions that depend on nucleotide composition. Overall, these results provide insights into the intermolecular interactions that occur between cationic amphiphiles and oligonucleotides, and thereby also provide guidance for the design of such complexes.

COLL 694

DNA-programmed polymeric micelles

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DNA-programmed polymeric nanoparticles are presented as stable nucleic acid delivery vehicles that facilitate communication with biological entities in a specific and predictable manner. Based upon the three-dimensional architecture and spatial arrangement of nucleotides at the surface-solution interface, these materials exhibit unique interactions with biologically relevant constituents such as enzymes, proteins and cell membranes. These interactions can be tuned by structure and sequence in order to provide a promising class of information-rich materials.

COLL 695

Aggregation behavior of charged surfactants in ionic liquids

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Room-temperature ionic liquids (ILs) have been recently explored as extraordinary solvent with potential opportunities for numerous applications. We set out to obtain a better understanding of the aggregation behavior of charged surfactants within ILs. From phase diagrams and isotherms in several distinct ILs, a connection between solubility of the surfactant and the physical properties of the underlying ionic liquid was established. We conclude that the interfacial energy is crucial in determining aggregation behavior while electrostatic interactions can be largely ignored. This study was extended to include mixtures of cationic and anionic surfactants where our data further demonstrate near-complete charge screening. Mixtures of charged surfactants in ILs can therefore be considered as nearly ideal, in sharp contrast to aqueous solutions. The results here give insight into the nature of self-assembly of surfactants in ILs and the interaction between solutes and IL solvents.

COLL 696

Triply periodic, multiply continuous lyotropic liquid crystals derived from gemini dicarboxylate amphiphiles

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Rational design criteria for small molecule amphiphiles that reliably form technologically useful, triply periodic, multiply continuous aqueous lyotropic liquid crystals are not well-

established. Since these network phases (e.g., bicontinuous cubic gyroid and diamond morphologies) typically exhibit interfaces that significantly deviate from constant mean curvature, traditional single-tail surfactants only form these structures over small amphiphile concentration and temperature phase windows. We recently demonstrated the unusual propensity for anionic dicarboxylate gemini surfactants to form bicontinuous cubic lyotropic phases (Q-phases) over large amphiphile concentration windows up to 20 wt% wide between 25-100 °C. In the context of these studies, we describe the discovery and identification of a new triply, periodic multiply continuous, lyotropic network phase with non-cubic symmetry.

COLL 697

Surfactant, Polymer and Block Copolymer Templated Self-Assembly of Hierarchically Porous Materials

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Since the first reports of the formation of mesoporous silica templated by quaternary ammonium surfactants in 1992 soft-templating methods have grown rapidly in the range of materials and applications. The ability of surfactants and block copolymers to form a wide range of three-dimensional structures has given rise to a great diversity of mesoporous materials. Similarly the range of forms of the various materials has also expanded, from particles, to thin films and then to macroscopic monolithic pieces. The formation of structure at multiple length scales has become of interest for applications ranging from catalysis to energy generation and storage. By combining higher molecular weight polymers and surfactants into silica sol-gel and carbon precursor solutions it is possible to make porous monoliths with well ordered mesopores and macroporous networks. This presentation will illustrate examples of both these approaches and discuss the fundamentals of such methods and their extension to other materials.

COLL 698

Shape-Persistent Micelles Bearing Calix[4]arene Building Block

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A series of calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found that some of them form spherical micelles with a defined aggregation number. These aggregation numbers are 6, 8, and 12, interestingly coinciding the number of the Platonic solid. Synchrotron small-angle X-ray scattering (SAXS) patterns exhibited a sharp intensity dump, indicating high symmetry and shape monodispersity. The size monodispersity of the micelles was confirmed with analytical

ultracentrifugation. The present results indicate that a suitable combination of tail length, head volume, and rigidity of the building block is necessary to attain the shape persistency. With a shape determination program of Dummy and molecular dynamics calculation, the micellar architecture was determined.

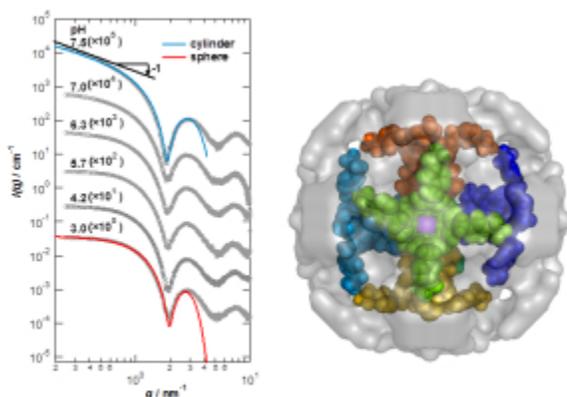


Figure 1 . SAXS profile changes upon pH change for CaL[4]C3 (left) and the result of the dummy bead and MD models

COLL 699

Photon Correlation Spectroscopy for Molecular Self-Assembly Investigations

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The molecular self-assembly performance is among the most important functionalities of amphiphilic compounds in colloidal system areas. This aptitude is required in numerous applications, depending on solubilization, hydrotropy, rheology, separation, loading and delivery, encountered in biological and industrial processes. The main physicochemical parameter predicting the capacity of amphiphiles to self-assembly in bulk liquid, aqueous (normal micelles) or non-aqueous phase (reverse micelles), is the pair critical micelle concentration (CMC) and temperature (CMT). A variety of methods based on surface tension, spectral changes, and electrical conductivity are commonly used for determining the value of CMC. The choice usually depends on the ionic or non-ionic nature of the amphiphilic compounds. In this communication, a standard Photon Correlation Spectroscopy (PCS), also known Light Scattering-based technique for CMC determination will be theoretically and practically described in details. Its particular

interest for measuring the performance of non-ionic and very high hydrophobic tail, mono or disubstituted carbohydrate-based compounds, from C16 alkyl chain, will be demonstrated. Such a method is advantageous regarding the time, amount, and resolution required, but also for additional information on micelle size, aggregate number, and stability it may provide, compared to surface tension and electrical conductivity-based measurements.

COLL 700

Micellar structure and adsorption behavior of a polystyrene-based block copolymer

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A near-monodisperse poly(styrene-hydrogenated isoprene) diblock copolymer (28 mol % styrene) prepared via anionic polymerisation forms well-defined polystyrene-core micelles in n-alkanes. The effect of varying the solution temperature on the copolymer micelle structure is studied using transmission electron microscopy, dynamic light scattering, ¹H NMR spectroscopy and small angle x-ray scattering. Direct dissolution at 20°C leads to meta-stable worm-like micelles; spherical micelles are formed on heating to 90°C, which are retained on cooling to 20°C. Adsorption of copolymer micelles onto carbon black is also examined. The presence of copolymer at the carbon black surface is confirmed by x-ray photoelectron spectroscopy. An absorption isotherm is constructed using a supernatant depletion assay based on uv spectroscopy to quantify the aromatic chromophore due to the polystyrene block at 262 nm. Evidence is presented for micellar adsorption from n-alkanes and unimer adsorption from chloroform, which is a good solvent for both blocks of the copolymer.

COLL 701

CO₂ Pre-activation via Charge Transfer States of TiO₂-Aminosalicylic Acid Complexes

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Salicylate and salicylic acid derivatives act as electron donors via a charge-transfer complex when adsorbed on semiconducting surfaces. When photoexcited, charge is injected into the conduction band directly from their highest occupied molecular orbital (HOMO) without

needing mediation by the lowest unoccupied molecular orbital (LUMO). In this study, we successfully induce the chemical participation of carbon dioxide in a charge transfer state using 3-aminosalicylic acid (3ASA). We determine the geometry of CO₂ using a combination of UV-vis, SERS, ¹³C NMR, and EPR. We find CO₂ binds on Ti sites in a carbonate form and discern via EPR a surface Ti-centered radical in the vicinity of CO₂, suggesting successful charge transfer from the sensitizer to the neighboring site of CO₂. This study opens the possibility of analyzing the structural and electronic properties of the anchoring sites for CO₂ on semiconducting surfaces and proposes a pathway for CO₂ remediation.

COLL 702

Design of early/late heterobimetallic complexes for CO₂ activation

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Early/late heterobimetallic complexes have long been thought of as molecular models of the interactions that occur between late transition metal catalysts and Lewis acidic metal oxide surfaces ("strong metal support interactions"). In light of this, early/late heterobimetallic complexes featuring highly polar dative M→M interactions are being targeted for applications toward catalytic CO₂ reduction. The metal-metal interactions in a Zr/Co model system have been shown to lead to a dramatic +1 V shift in reduction potential compared to monometallic Co analogues. This might suggest that similar interactions between late metal catalysts and Lewis acidic surfaces can also be used to tune redox potentials. Moreover, reduced Zr/Co heterobimetallic complexes have been shown to rapidly cleave CO₂ into a late metal carbonyl (Co-CO) and early metal oxo (Zr-O) fragment. Progress towards understanding the catalytic implications of this reaction and the design of new early/late heterobimetallic systems will be discussed.

COLL 703

All-inorganic polynuclear units in silica scaffolds for carbon dioxide photoreduction

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Our objective is to develop inorganic photosynthetic units that afford closing of the cycle for carbon dioxide reduction by water to a fuel in a nanoscale system. The building blocks are inorganic bi- and polynuclear structures as light absorbers and catalysts, and nanoscale silica layers for product separation. Chromophores are oxo-bridged binuclear structures such as ZrOCo(II) or TiOCr(III) covalently anchored on the silica surface.

ZrOCo sites afford visible light induced reduction of CO₂ to gas phase CO and formate. Discovery of visible light sensitized Co₃O₄ nanoclusters on mesoporous silica as efficient water oxidation catalysts under neutral pH conditions has opened up the exploration of a Co₃O₄/SiO₂ core/shell nanotube design for closing the photosynthetic cycle under separation of products.

COLL 704

Influence of photodeposited gold nanoparticles on the photocatalytic activity of isolated titanate species in the reduction of CO₂ to hydrocarbons

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Anpo's pioneering single site titanate catalysts are still the most studied photocatalysts for CO₂ reduction. However, there is a need to greatly improve the overall activity. In this contribution, we show that a modification of isolated titanate species on SBA-15 by photodeposition of gold nanoparticles can increase the photocatalytic activity and alter the selectivity pattern. The performances gold-loaded and gold-free samples were compared in a fully-metal sealed stainless steel reactor allowing thorough pre-cleaning of the materials. While no product formation was detected without catalyst, the formation of methane and longer chain hydrocarbons (C1 to C4) was observed with both catalysts. The product distribution indicates that hydrogenation activity is improved in presence of Au. Under reaction conditions with CO₂ excess, carbon-containing species were stored on the catalyst surface, especially on the gold-free sample.

COLL 705

Development of an Artificial Z-scheme for Photocatalytic Reduction of CO₂

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A hybrid for visible-light-driven photocatalytic reduction of CO₂ with methanol as a reductant was constructed by combining two different types of photocatalysts, i.e, a Ru(II) dinuclear complex for CO₂ reduction adsorbed on Ag-loaded TaON (**TaON-Ag**) for oxidation of methanol. The isotope experiments clearly showed that this hybrid photocatalyst mainly produced HCOOH from CO₂ and HCHO from methanol. The photocatalytic reaction proceeds via stepwise excitation of both **TaON-Ag** and the Ru dinuclear complex on **TaON-Ag** like the Z-scheme of photosynthesis of green plants.

COLL 706

Metal Organic Frameworks for water oxidation and CO₂ and Proton Reduction

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Integration of individual molecular components in a structurally controlled manner remains one of the challenges of artificial photosynthesis. Metal organic frameworks (MOFs) can serve as such a platform to integrate different functionalities. We have incorporated catalytically competent Ir, Re, and Ru complexes as dicarboxylate ligands into highly stable and porous UiO frameworks. The resultant MOFs were active catalysts in a range of reactions that are relevant to solar energy utilization, such as water oxidation, photocatalytic proton and CO₂ reduction and organic transformations. Taking advantage of site-isolation of the immobilized catalysts and the heterogeneous nature of MOF, we were able to perform studies that are not possible in homogeneous systems. With hierarchical design, we achieved synergistic operation of different components in the same framework, leading to enhanced light harvesting efficiency and photocatalytic activity. The presented work illustrates the potential of combining molecular catalysts and MOF structures in developing systems for solar energy utilization.

COLL 707

Early metal hydride, nitride, and oxide approaches to CO₂ activation

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While exploring the chemistry of niobaziridine and tantalaziridine hydride complexes we observed that CO₂ uptake to form methylenediolate, a ligand frequently invoked as an intermediate in heterogeneous CO₂ reduction systems, takes place by way of formate intermediates. In addition, we have developed a cycle for CO₂ reduction to CO that takes place at a terminal nitride ligand without initial complexation of CO₂ at the transition metal. Extending the latter mode of CO₂ activation to an oxide platform, we found that CO₂ binding to a terminal oxoanion complex of titanium could be both reversible and tuned by proper selection of the alkali-metal counter-ion. Finally, investigation of CO₂ binding to other molecular oxide systems will be discussed with reference in particular to possible applications in catalysis.

COLL 708

Surface-Immobilized Transition Metal Complexes for Photocatalytic CO₂ Reduction

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Carbon dioxide is a renewable carbon feedstock for the production of chemicals, materials, and fuels. Photochemical reduction is a sustainable approach to achieve CO₂-to-fuel conversion. Our current research focuses on surface immobilization of transition metal complexes on mesoporous silica for use in CO₂-reduction catalysis. The current status of CO₂-reduction catalysis using innovative photocatalysts will be briefly reviewed. This presentation will then introduce our recent results on CO₂ reduction using tricarbonyl Re(I) and macrocyclic Ni(II) complexes. Our research highlights the advantages of integrating well-defined molecular catalysts with robust solid-state surfaces in solar energy applications.

COLL 709

Targeted TERS: Using functionalized nanoparticles to guide tip-enhanced Raman investigations

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Noble metal nanostructures are known to give rise to large enhancements in the Raman scattering observed from molecules in close proximity. Tip enhanced Raman (TERS) microscopy utilizes a nanostructure scan-probe tip to spatially detect the distinct Raman scattering from molecules at the nanoscale. Challenges in the use of TERS for biological investigations include knowing what region to probe and generating sufficient signal. Targeted TERS is methodology we have developed that seeks to address both these challenges. We have coupled TERS with nanoparticle probes to obtain chemical, structural, and spatial information simultaneously from phenomena such as protein-ligand interactions. Individual nanoparticle probes are detected using dark-field microscopy, identifying regions to investigate with high spatial resolution TERS microscopy. Raman enhancements are known to be greatest in dimers and other aggregates, thus the combination of the nanoparticle with TERS tip generates a local dimer-structure, increasing the Raman signal detected. We have demonstrated the ability to detect functionalized nanoparticles bound to proteins on surfaces and to cellular membranes. In this presentation we will discuss our methodology and its application to specific biomolecular systems.

COLL 710

Tunneling spectroscopy of benzoic and phosphonic acid monolayers: The role of the metal-molecule interface

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A series of self-assembled monolayers were prepared from para-substituted benzoic and phosphonic acids onto oxidized Al films and characterized by XPS and contact angle measurements. The acids adsorb to the oxide as a carboxylate or phosphonate group with the plane of the aromatic ring largely perpendicular to the surface, which places the para-substituent away from the surface. XPS and contact angle measurements confirm phosphonic acid monolayers pack more densely than benzoic acid monolayers. Tunnel junctions were made by vapor deposition of Au and Pb films as the top electrodes onto the monolayers. Tunnel junctions made without SAMs showed large shifts of the in the $G(V)$ minimum [$G(V)_{\min}$] conductance. Upon addition of the phosphonic acid and carboxylic acids monolayers, the $G(V)_{\min}$ shifted closer to zero, due to the polar hydroxyl groups being replaced by the less polar SAMs. Further details of this work will be discussed in this talk.

COLL 711

Ion Concentration Polarization in Single Conical Nanopores – Charge Balance at Nanoscale Interfaces

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Concentration polarization is a fundamental phenomenon that occurs at charge-selective interfaces, such as electrode surfaces and micro or nanochannel interfaces. The concentration gradient at a nanoscale interface, well known to differ from macroscopic double layer, induces many important and fascinating phenomena. Interesting pinched hysteresis loops with a non-zero cross point are found in current-potential curves in the study of the ionic transport through single conical nanopore under a cyclic sweeping potential. The accumulated charges in each hysteresis loop are quantified under different potential scan rates or in different electrolyte concentrations. Both experimental and theoretical results show that this concentration polarization process can be described by simple in-series RC equivalent circuits. The calculated polarized charge distribution quantifies the concentration polarization at nanoscale interfaces, which has been applied in various fields such as molecular concentrator, precipitation or crystallization, sensing and separation.

COLL 712

Molecular Dynamics Simulations of Nanoparticle Self Assembly at Ionic Liquid-Based Interfaces

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Ionic liquids, with their unique composition, present a new kind of liquid-liquid interface which is not yet well understood. We have studied the self-assembly of hydrophobic and hydrophilic nanoparticles at ionic liquid (IL)-water and IL-oil (hexane) interfaces using molecular dynamics (MD) simulations and potential of mean force studies. Using 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) as a model IL, we observed that particles interacted with the liquid-liquid interface in a tunable manner. Their self-assembly depended primarily on particle charge, surface chemistry, and interface type (water or oil). Potential of mean force (PMF) calculations supported the observations from the equilibrium studies and correlated reasonably well with continuum models and experimental measurements. We also show how ILs adapted to form solvation layers around immersed particles of different surface chemistries. Such solvation layers varied in morphology and dynamics in response to hydrophobic and hydrophilic surfaces.

COLL 713

Effect of functional group and saturation level on miscible and partially miscible systems

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In this study, we evaluated the effect that functional group and saturation level might have on IT (interfacial tension) and on the behavior of three different types of partially miscible and miscible systems. With the pendant drop method, we measured IT at different temperatures and saturation levels. We observed different behaviors for these systems including end pinching and sharp concentration gradients. IT was affected by saturation of different phases and functional group. The aqueous phase had more impact on IT than the lighter phase. In conclusion, functional groups had an effect on LCST and IT but not on behavior. Behaviors were unique to types of miscible and partially miscible and but not to functional groups. Finally, we conclude that type of miscible and partially miscible system can be critical in assessing behaviors and IT of these systems.

COLL 714

Self-ordered bent-core liquid crystals in surface modified porous alumina nanochannels

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Self-assembled bent-core mesogen exhibit novel structural properties such as polar, liquid-crystalline order and interplay of chiral even they are achiral molecules. Among the chiral layered phases, twisted helical nanofilaments can be formed in B4 phase with a macroscopically chiral structure and maintained by the long-range continuity of the smectic layers. Some research groups have investigated that the helical nanofilaments grew in from the B2 phase and branch off from existing ones forming large chiral domain with fan-shaped conformation due to their helical structure in bulk state. Here, we obtained individual helical nanofilament maintaining their straightness regardless of their helicity confined in porous alumina nanochannels. Furthermore, the molecular orientation in isotropic phase can be controlled by chemical surface modification. Depending on chemical affinity such as hydrophobicity and hydrophilicity, molecules take on an orientation perpendicular or parallel to the surface. In sequence, layer direction in smectic mesophase affected by the orientation of liquid crystal molecules and as a result, helical nanofilaments and nanodisk mesophase transformation can be naturally formed merely depending on surface chemical properties with same mesogen. We investigated the molecule orientation confined in surface modified porous alumina thin films by electron microscope and x-ray analysis. Electron microscope cross section images of the liquid crystals in surface-modified nanochannel revealed the tendency and correlation between the surface energy and the morphological conformation of smectic layers in liquid crystals. GIXD (Grazing incidence x-ray diffraction) analysis also informed the details of molecular orientation, the direction of alignment and d-spacing of layers. Our approaches on thin film analysis of bent-core liquid crystal confined in chemically modified AAO nanochannel will be helpful for improved understanding of the fundamental studies on B-phase and lead to the development of basic designing principles to achieve spontaneous bent-core based materials with simple chemical treatments.

COLL 715

Surface-specific vibrational spectroscopy of synthetic secondary organic aerosol particles and their precursors

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Isoprene and alpha-pinene are abundant volatile organic compounds (VOCs) that are emitted by trees and oxidized in the atmosphere. We have synthesized proposed products of isoprene and alpha-pinene oxidation and the oligomers that form from them. We utilize vibrational sum frequency generation (SFG) spectroscopic studies, which allow us to assess the surface chemical identity of aerosol-forming components on a molecular level, with the ability to control their stereochemistry. Since many VOCs are chiral, and chirality is known to influence materials properties, we explore the possibility

of stereochemical transfer to atmospheric aerosol particles during the oxidation of biogenic VOCs. The spectral responses from these compounds are compared to those of synthetic isoprene- and alpha-pinene-derived aerosol particles, as well as natural aerosol particles. In addition, isotope editing is utilized in a combined theoretical, synthetic, and spectroscopic approach to better understand the surface orientation of alpha-pinene, as well as its oxidation chemistry.

COLL 716

The “pH Transparency” of CVD Graphene Studied with Second Harmonic Generation

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A detailed molecular level understanding of the interfacial structure between water and graphene is needed in order to understand electron transfer reactions that occur at the fluid/solid interface. Here, second harmonic generation (SHG) is employed to investigate the interfacial environment over single- and multi-layered chemical vapor deposition (CVD) graphene sheets supported on a fused silica substrate. We find no alternation of the acid-base chemistry occurring at a fused silica/water interface when single-layer or 8-layer graphene is placed in-between the silica and aqueous phase, as monitored by pH dependent SHG measurements. This apparent pH transparency of graphene could be due to diffusion across grain boundaries and other defect sites as quantified by ab initio simulations, scanning transmission electron microscopy (STEM), and scanning electron microscopy (SEM).

COLL 717

Spectro-Microscopy investigations of designed 'Spin-terfaces', controlled by on-surface coordination chemistry

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Biochemistry, University of Bern, Bern, Switzerland (5) *Swiss Light Source, Paul Scherrer Institute, Villigen PSI, Switzerland* (6) *Department of Chemistry, Indian Institute of Science Education and Research (IISER), Pune, India*

Paramagnetic metal-organic complexes on ferromagnetic surfaces are of significant interest for potential applications in organic spintronics. We study the magnetochemical interactions at tunable “spin-terfaces” by combination of Scanning Tunneling Microscopy (STM) and element specific X-ray Magnetic Circular Dichroism (XMCD).

On-surface coordination chemistry in conjunction with a bottom-up approach is employed to fabricate highly ordered two dimensional layers of Fe and Mn complexes. The ferromagnetic substrate induces a magnetic moment into the Fe and Mn ions at room temperature. The selective response of the Fe and Mn spin-systems towards axial coordination with ammonia allows for the reversible switching of the magnetic moments in the Fe-Mn-Fe chess-board lattice. High resolution STM also yields direct visualization of the axial ammonia-coordination.

COLL 718

Ionic Content of Polyelectrolyte Multilayers

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The buildup of multilayer thin films of poly(diallyldimethyl ammonium) (PDADMA) and polystyrene sulfonate (PSS) was investigated. The actual amount of extrinsic charge compensation in the polyelectrolyte multilayer film was measured by using radiolabeled counterions. Measurements were made on films built at different salt concentrations by the layer-by-layer assembly technique. Fourier Transform Infra-Red spectroscopy (FTIR) and X-Ray Photoelectron Spectroscopy (XPS) were also used to provide quantitative analysis on bulk and surface counterion content. It was found that there were far more positive extrinsic charges when the films were terminated with PDADMA than there were negative extrinsic charges when the films were terminated with PSS. After a specific number of layers deposited, depending on the salt concentration used during the buildup, positive extrinsic charges started to immobilize in the bulk of the film. Thus, it appears that most of the critical overcompensation in these multilayers is done by PDADMA and not by PSS

COLL 719

Tough double network hydrogels as antifouling materials

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The adhesion of marine sessile organisms is often found on submerged solid surface such as rocks, metals, plastics, etc. while there is no adhesion on the surface of marine livings, such as seaweeds, that are in soft and wet “hydrogel” state. Inspired by this fact, we studied antifouling properties of hydrogels against marine sessile organisms. Hydrogels, especially hydrogels with hydroxy group and sulfonic group, show excellent antifouling activities against barnacle both in laboratory assay and in long-term marine environment. We have elucidated that the extreme low settlement on hydrogels *in vitro* and *in vivo* are caused mainly by antifouling properties against barnacle cyprids. Based on these results, we developed tough double network hydrogels as antifouling materials.

COLL 720

The effect of substrate topography on marine adhesion

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We will discuss the combined effect of the size, chemistry and orientation of buckles arranged into hierarchical assemblies on the settlement of barnacle cyprids. The settlement process involves a complex interplay between the aforementioned phenomena, revealing that the best substrates comprise hydrophobic layers bearing wrinkles whose sizes are comparable to that of the cyprid. We also report on a simple Monte Carlo model to simulate the adhesion of spherical particles with sticky polymeric hairs (i.e., synthetic mimics of biological organisms) on a variety of surfaces that possess sinusoidal variation of amplitude and periodicity in an effort to design the optimal set of surface attributes. We study adhesion of particles with varying diameter and the number and length of hairs on a range of sinusoidal periodic surface structures. This approach allows us to establish the optimal surface parameters minimizing the adhesion of particles with varying properties.

COLL 721

Responses of settling marine fouling organisms to nanopatterned surfaces

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The early settlement stages of marine biofouling organisms are often poorly understood. We present results on how surfaces that have nanoscale patterned surface energies affect organismal settlement. Information on settlement preference, adhesives released and strength of adhesion will be presented. Methods to prepare robust model surfaces will also be presented.

COLL 722

Chemical cues guide exploration and settlement of marine fouling organisms

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Colonization of surfaces by biofouling organisms usually occurs through their dispersal stages. This could be the planktonic stage of bacteria or, for larger organisms, spores or larvae. The selectivity during this dispersal stage is crucial for the long-term fate as it decides on secure anchoring and germination on the surface. Especially the three-dimensionality of the exploration process requires holographic or stereoscopic techniques, which are capable to record the full 3D scenes with video frequency. This allows quantitative analysis of exploration and settlement behavior. By this we obtain quantitative access to the interaction between single organisms and chemically functionalized surfaces. The obtained results are discussed in the context of physicochemical surfaces properties (e.g. hydration, surface energy, and steric repulsion), time depending formation of conditioning layers, and the mechanism used for surface selection. Based on these design rules, non-toxic antifouling surfaces on the basis of natural polymers are developed.

COLL 723

Towards Thermally Robust SERS Substrates for High Temperature Sensing

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We have fabricated thermally robust surface enhanced Raman spectroscopy (SERS) substrates with Au and Ag nanoparticles that maintain their discrete size and distribution upon exposure to high temperature. Nanoparticles were immobilized on a porous anodized aluminum oxide (AAO) template and heated to 200°C, 300 °C, and 400 °C for 15 minutes. The substrates were characterized at room temperature with SERS, SEM and XPS after heat treatment. Trapping nanoparticles in the pores of AAO prevented the coalescence of colloids at elevated temperatures, preserving their LSPR and SERS activity. The enhancement factors (EF) increased gradually with increasing temperature due to desorption of stabilizing and reducing agent and hence more binding sites for analyte (R6G). The results will be interpreted in terms of temperature-induced changes in the particle distribution and surface chemistry of both Au and Ag nanoparticles based on the SEM, XPS and SERS studies.

COLL 724

Robust and Reproducible Quantification of SERS Enhancement Factors using Combination of Time-resolved Raman Spectroscopy and Solvent Internal Reference

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Recent research demonstrates that SERS substrate modifies analyte Raman signal through two competitive mechanisms: SERS enhancement and substrate inner filter effect, not SERS enhancement alone as commonly believed. Using combination of time-resolved Raman spectroscopy and solvent internal reference method, reported herein is quantitative determination of SERS EFs of mercaptobenzimidazole (MBI), a model organothiols adsorbed onto AuNPs and AgNPs. The peak MBI SERS EF depends only on the types and sizes of nanoparticles, but not on other experimental conditions we explored (analyte and AuNP concentrations, and the type and concentrations of the electrolytic aggregation agents (KF, KCl, KBr, and K₂SO₄)). The experimental peak SERS EFs of MBI on AuNPs and AgNPs with sizes of 30 and 50 nm can be fully explained with electromagnetic mechanism alone. This result, in combination of our recent finding that a series of highly structurally organothiols have similar SERS EFs, argue strongly against the possibility of strong chemical enhancement (>10 times, for example) for organothiols adsorbed onto colloidal AuNP and AgNP.

COLL 725

Size-specific, few-atom Ag cluster fluorophores

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Fluorescence imaging in biological and medical sciences is often hindered by significant depth-dependent signal attenuation and high fluorescent backgrounds. Nanotechnology offers significant opportunities for signal gains when using, for example, quantum dots or plasmon-enhanced emitters, but significant size, bioconjugation, toxicity, and aggregation concerns become paramount. We have addressed the limited brightness and biocompatibility issues in fluorescence imaging by encapsulated highly fluorescent metal nanoclusters, consisting of fewer than 12 silver atoms. These species show excellent brightness and great promise in both single molecule and bulk imaging, while maintaining small overall size. Still, these species are insufficiently bright for the most demanding applications. Their unique photophysics, however, has enabled optical modulation of their emission that not only increases total emission, but, more importantly, greatly reduces background. Demodulation of nanodot signals enables fluorescence image recovery from within high backgrounds, resulting in order-of-magnitude sensitivity increases. Our detailed studies of the states enabling low-energy optical modulation have enabled us to both approach biosensing and biolabeling

applications and translate these concepts to more standard organic fluorophores. These general concepts of removing background through selective fluorescence modulation are applicable to a wide variety of systems, with Ag nanodots and modulatable organic dyes being used for a variety of detection and imaging applications.

COLL 726

Spectroelectrochemical Studies of Single Ag Nanostructures via Fluorescence Spectroscopy and Dark Field Scattering

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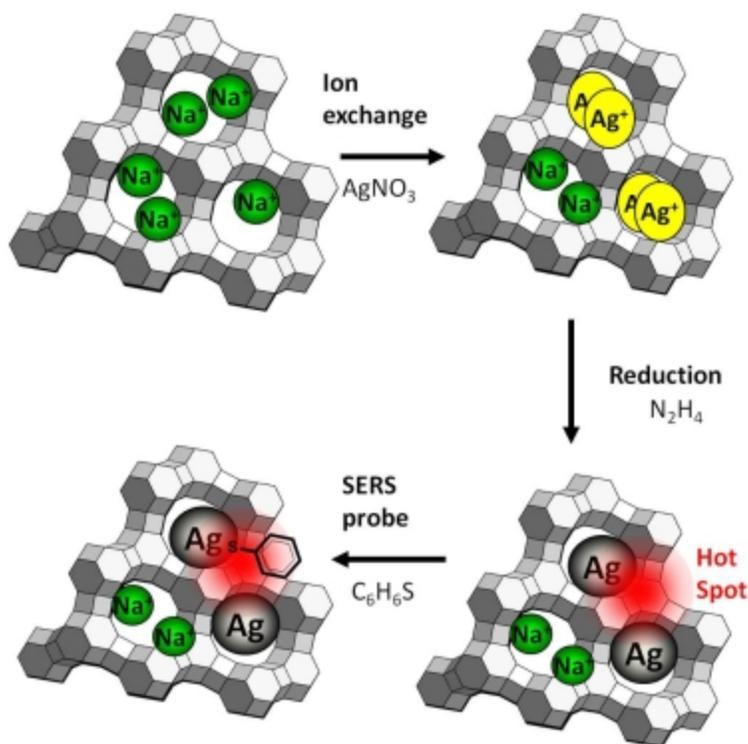
Single-nanoparticle spectroelectrochemical (SNP-SEC) studies of Ag nanoparticles (NPs) are presented. The electrochemical oxidation of single, pre-synthesized, fluorescent Ag NPs was visualized via fluorescence studies. Additionally, the electrochemical properties of Ag NPs synthesized in-situ via the reduction of Ag⁺ were also investigated via fluorescence and dark field scattering. In both cases, heterogeneities in the reaction half potentials for single nanoparticles obtained via optical measurements were observed which were not visible in the direct electrochemical measurements.

COLL 727

Evolution of silver particles in nano-sized zeolite via chemical reduction

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Nanometer –sized three dimensional zeolite Y (FAU) type aluminosilicates with open frameworks are used as templates to synthesize closely spaced silver nano-particles, via chemical reduction. Kinetic control of the reduction process results in ~2nm silver particles dispersed throughout the zeolite host crystal. The resulting 40nm zeolite crystals loaded with silver is explored as a SERS active substrate, and correlations between SERS enhancement and microstructure is developed.



COLL 728

TERS and SERS: Different Raman enhancements from different nanostructures

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Nanostructures give rise to significant enhancements in the Raman scattering observed from molecules in close proximity. This electromagnetic field enhancement has transformed Raman into an ultra-sensitive method of analysis. Since Raman is a label-free technique, these enhancements enable detection and identification of a wide range of molecules and interactions. Our research utilizes these enhancements for both imaging and trace analyte detection in biological systems. We have coupled tip-enhanced Raman scattering (TERS) with nanoparticle probes to obtain chemical, structural, and spatial information simultaneously from phenomena such as protein-ligand interactions. Additionally we have developed nanostructured surfaces that enable high signal to noise Raman measurements on millisecond time scales. In this presentation we will discuss the differences in signals that we observe as an increasing numbers of nanostructures interact together. We will examine differences in the signals observed from an isolated nanostructure (a TERS tip), tip-nanoparticle dimers, nanoparticle aggregates, and nanostructure arrays. Differences in the observed signals support a model where the observed vibrational modes vary with nanostructure complexity.

COLL 729

Unveiling plasmon delocalization and ultranarrow resonances in rough silver films with single nonlinear hot spots

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The naturally disordered rough silver films that are grown with the Tollens silver mirror reaction provide a fascinating plasmonic platform that unites fundamental phenomena with practical utility. The extraordinary optical enhancement factors that result from their complex resonances enable single molecule surface-enhanced Raman (SERS) studies as well as an amplified, intrinsic nonlinear response. Under pulsed infrared excitation, supercontinuum emission and second-harmonic generation are observed from discrete nonlinear hot spots, which can be used as facile far-field, background-free probes of the plasmon resonances. Structure-property relationships between the plasmons and film morphology can be unraveled by combining single nonlinear hot spot spectroscopy with electron microscopy of films with varying surface coverage. Upon transitioning from spatially localized resonances of nanoparticles to delocalized resonances of larger metal structures, the single nonlinear hot spots exhibit multiple extraordinarily narrow resonances with line widths as small as 7meV, two orders of magnitude narrower than the supercontinuum generated.

COLL 730

Plasmonic Transducers Studied by Single-particle Nonlinear Optical Spectroscopy

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We report nonlinear optical (NLO) spectroscopy experiments carried out at the single-particle to probe nanoparticle surface plasmon fields. As one example, we report the observation of magnetic dipolar contributions to the NLO response of colloidal solid gold nanosphere (SGN) dimers. Second-order NLO responses from these dimers were examined using polarization-resolved second harmonic generation (SHG) spectroscopy at the single-particle level. Unambiguous circular dichroism in the SHG signal was observed for many of the structures, indicating the presence of a chiral plasmon field within the interparticle gap. Detailed analysis of the polarization line shapes of the SHG intensities obtained by continuous polarization variation suggested that the effect resulted from strong magnetic dipolar contributions to the nanostructure's optical properties. The relative magnetic-dipolar and electric-dipolar contributions to the NLO response were structure dependent, an effect that would have been obscured for

ensemble measurements. These findings may be significant for applications using the plasmonic nanostructure platform including nanoantennas, metamaterials, biosensing and energy conversion.

COLL 731

Biomimetic membranes in basic science and application

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Much cell-cell communication is mediated by proteins and processes located at the plasma membranes of the participating cells. Thus, biomimetic membrane surfaces have been recognized for many years as an ideal tool to study such communication processes or to create active, biocompatible interfaces with living cells. However, much about the basic membrane –cell interactions in such systems is unknown. Furthermore, reliable and general schemes to decorate artificial membranes with the necessary proteins for cell attachment and communication remain a challenge. Here, we present results that elucidate the cellular responses to biomimetic membranes of different properties. In addition, a modular scheme for protein augmentation of membranes that is based on site specific lipidation is discussed.

COLL 732

Biomaterial-induced protein unfolding as a universal mechanism controlling blood compatibility

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Although it is widely believed that blood compatibility is primarily determined by the amount of fibrinogen adsorbed to a biomaterial surface, recent results in our laboratory have shown that platelet adhesion does not generally correlate with the amount of adsorbed fibrinogen but with the degree of biomaterial-induced protein unfolding. Our studies have shown that platelets will even readily adhere to adsorbed albumin through this mechanism. We have further proved that platelet adhesion to albumin is actually receptor mediated, even though albumin has no known platelet binding sites. We hypothesize that the mechanism responsible for this behavior is the pulling apart of salt bridges between oppositely charged amino acid residues, such as arginine and aspartic acid, thus creating RGD-like motifs and that this is a universal response for all proteins. In this talk I will present our experimental results that support these hypotheses and their implications for biomaterial surface design.

COLL 733

Enzymatic activity of cholesterol oxidase immobilized onto polymer nanoparticles mediated by Congo red

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Poly(ethylene glycol), PEG, decorated nanoparticles of polystyrene (PS) were synthesized and characterized by means of dynamic light scattering (DLS), zeta (ζ) potential, infrared vibrational spectroscopy with Fourier transform (FTIR) and scanning electron microscopy. The adsorption of Congo red (CR) onto PS/PEG particles was evidenced by the decrease of ζ potential values, the increase in the mean diameter and FTIR. Cholesterol oxidase (ChOx), the main enzyme in the oxidation of cholesterol, adsorbed onto PS/PEG and PS/PEG/CR particles, as evidenced by the increase in the particles mean size and spectrophotometry. The enzymatic activity of free and immobilized ChOx was determined as a function of time by means of a coupled reaction with horseradish oxidase. The immobilization on PS/PEG/CR improved the enzyme stability in comparison to free ChOx. Freeze-drying the ChOx covered PS/PEG/CR particles allowed their storage under room conditions without loss of enzymatic activity. The favorable interactions between CR and ChOx or cholesterol were evidenced by circular dichroism and spectrophotometry. ChOx adsorbed onto PS/PEG presents no enzymatic activity due to the difficult access of cholesterol to ChOx. A general model is proposed in order to achieve catalytic efficiency of immobilized enzymes. It comprises the preservation of enzyme natural conformation, adequate orientation of active site and the appropriate surface energy (or hydrophilic/hydrophobic character). The supporting material hydrophobic/hydrophilic character should match that of the substrate to enable the accessibility of substrate to the active site of immobilized enzyme.

COLL 734

Role of physicochemical properties on biofilm eradication for nitric oxide-releasing nanomaterials

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Nitric oxide (NO) is a reactive free radical that exhibits broad-spectrum antibacterial properties due to multiple mechanisms of action. Recent work has focused on the development of NO-releasing macromolecular scaffolds (e.g., nanoparticles and dendrimers) to combat bacterial biofilms. Developing an understanding of how a scaffold's physicochemical properties influence biofilm eradication is essential for optimizing its anti-biofilm efficacy. Herein we report the effects of nanoparticle composition, size, shape, and surface hydrophobicity on the eradication of *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and dual-organism (i.e., *P. aeruginosa* and *S. aureus*) biofilms. In addition to the influence of these properties on

NO-mediated anti-bacterial activity, particle–bacteria association, intracellular NO concentrations, and cell death were visualized using confocal microscopy.

COLL 735

In Vitro and Ex Vivo Toxicology of Antimicrobial Conjugated Electrolytes: Interactions with Mammalian Cells

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Certain cationic phenylene ethynylene (CPE)-based polymers (PPEs) and oligomers (OPEs) exhibit dark- and light-activated antimicrobial activity. Until recently, it was unknown if they would also exhibit similar biocidal activity toward mammalian cells. Based on their biocidal activity and diversity of repeat unit number and functional groups, a variety of CPEs, PPEs, and OPEs were selected for these studies, and were examined for their toxicity toward mammalian cells at three levels: cytotoxicity testing of cell monolayers, skin irritation testing of tissues, and intracellular co-localization. As expected, concentration plays the largest role in determining viability. The lack of skin irritation for all substances alleviates initial safety concerns for products based on these CPEs and OPEs. In all cases, the addition of light changed the effects of the compounds on the mammalian cells. The modes of action of these compounds appear to be governed primarily by length.

COLL 736

New insights in protein-based nanoparticle agglomeration: Size characterization of nanoparticle-protein agglomerates in biological relevant environments

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Nanoparticles in physiological media are prone to form protein-coronae^[1] and agglomerates due to high salt contents and abundant biomolecules. Depending on the nature of colloidal stabilization, particle characteristics may be affected especially with respect to particle size, which plays a crucial role in terms of biodistribution^[2] and cellular uptake pathways^[3].

We demonstrate the impact of size and surface stabilization of silica- and poly(organosiloxane) nanoparticles to agglomeration at physiological conditions, using Dynamic Light Scattering (DLS), Analytical Ultracentrifugation (AUC) and Asymmetrical Flow-Field Flow Fractionation (AF-FFF). Measurements were accomplished in RPMI cell medium in presence of serum proteins, analogue to *in vitro* testings.

We observed amorphous silica NPs to form agglomerates depending on the size of the silica nanoparticles, whereas glycine stabilized poly(organosiloxane) NPs featured a thin protein corona. In contrast, PEGylated poly(organosiloxane) NPs were found to adsorb nearly no protein determined by a lack of change of hydrodynamic radii.

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[3] J. Kasper, M. I. Hermanns, C. Bantz, O. Koshkina, T. Lang, M. Maskos, C. Pohl, R. E. Unger, C. J. Kirkpatrick, Doi: 10.1007/s00204-012-0876-5.

COLL 737

Charged gold nanoparticles with essentially zero serum protein adsorption in undiluted fetal bovine serum

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Efficient renal clearance is typically required of gold nanoparticles used for in vivo biomedical applications. However the adsorption of even a single protein molecule can increase the particle size past the ~5.5 nm threshold required for clearance. Therefore, we have developed ~5 nm gold nanospheres with a mixed-charge ligand surface which completely prevents protein adsorption in undiluted fetal bovine serum (FBS). The moderately-charged nanospheres are comprised of an uneven ratio of anionic citrate and one of two naturally-occurring amino acids, either cationic lysine or zwitterionic cysteine. Dynamic light scattering (DLS) analysis on the particles shows no size increase after nanosphere incubation in 100% FBS indicating negligible protein adsorption. These same nanospheres were also assembled into ~20 nm, high near-infrared absorbing clusters via a biodegradable PLA-b-PEG-b-PLA polymer. After polymer degradation, the clusters dissociated back to original ~5 nm primary constituent nanospheres, which also did not exhibit serum protein adsorption.

COLL 738

Radiolabelling strategies for characterizing nano-particles: optimizing their design and engineering for biomedical applications.

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Functionalised nanoparticles are a new class of agents for the treatment of disease. Properties such as charge, size and, surface reactivity affect their ability to target and deliver their payload. We have adapted techniques used in nuclear imaging to understand functional properties of nanoparticles, an effort to optimise their engineering and *in vivo* behaviour. The hexa-aza bicyclic cage 1-*N*-(4-aminobenzyl)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane-1,8-diamine (SarAr) was first designed for ⁶⁴Cu positron emission tomography (PET) imaging and ⁶⁷Cu radiotherapy. The hexa-aza cages form extraordinarily stable and specific (1:1) complexes with metals and their radioisotopes. They are a highly sensitive tool that provide accurate information about the functional groups on particles and quantify their distribution *in vivo*. We present the use of SarAr and the new SarAr-NCS for characterising a range of polymeric and silica particles and how they can assist in the design functional nanoparticles for applications in drug risk assessment and radiotherapy.

COLL 739

Sonochemically made protein and nucleic acid nanospheres and their applications

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Sonochemistry is the research area in which molecules undergo chemical reaction due to the application of powerful ultrasound radiation (20 KHz–10 MHz). The ultrasonic waves have been applied for the synthesis of proteinaceous microspheres and non-protein nanospheres. Protein microspheres are today being considered for use in pharmaceutical and cosmetic areas providing microscopic biodegradable capsules for "smart" delivery of drugs and perfumes. In addition, for the first time, in the current research we have succeeded to convert native DNA and RNA molecules into nanospheres. The produced RNA and DNA nanospheres were found extremely stable at elevated temperatures and harmful conditions. Moreover, DNA and RNA nanospheres were successfully introduced into cancer cells and showed excellent gene expression results (in the case of DNA nanospheres) and gene silencing results (in the case of RNA nanospheres). In my thesis, the following types of microspheres are discussed: Mixed protein microspheres (microspheres made of a few different proteins), tetracycline (broad spectrum antibiotic) microspheres and attachment of those particles in to polyester fabrics, sonochemical nanospherization of DNA and RNA molecules.

Mixed proteinaceous microspheres (MPMs) have shown potential for imaging since a natural fluorescent protein was used (Green Fluorescent Protein and Cyan Fluorescent Protein-Glucose Binding Protein-Yellow Fluorescent fused protein) along with a common matrix BSA protein. The encapsulation of tetracycline with PMs and their use as a matrix capsule makes them particularly suitable for prolonged-release of antibiotic in a uniform dispersion. The perspective is to use these coated fabrics, inter alia, as antibacterial bandages in patient susceptible to contamination. Coated fabrics have also potential applications as: antibacterial textiles, textiles coated with microspheres containing inks or perfume and others.

COLL 740

Production and characterization of BSA nanospheres for drug delivery

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Protein nanospheres have a huge potential as possible vehicles for drug delivery due to their proven biocompatibility and biodegradability, sustained release, increased drug stability and targeting of specific tissues. In this study, we have produced several formulations of bovine serum albumin (BSA) nanospheres using a high-pressure homogenizer. Different parameters were optimized in order to obtain monodisperse formulations of small nanospheres, which are compatible with a potential application as drug delivery systems. The different formulations were extensively characterized and *in vitro* tests were performed. The incorporation of targeting and imaging agents and the encapsulation of drugs in nanospheres were also performed. Specific internalization and effect of drugs encapsulated in small BSA nanospheres obtained indicated that these protein nanospheres exhibit suitable characteristics for application as drug delivery systems.

COLL 741

Poly(N-vinylcaprolactam) nanogels with polyethyleneglycol shell: Tailoring nanomaterials by soap-less emulsion polymerization

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Nanogels have attracted growing interest owing to their potential application in drug delivery systems. Among the methods for preparation of nano/micro-gels micro-emulsion is simple to follow and may control the size of the nano/microparticles prepared. However the large amount of tensoactive compounds “soaps” needed to achieve the control are unacceptable for biomedical applications. In this work, temperature responsive nanogels based on the biocompatible polymer poly(N-

vinylcaprolactam) (PNVCL) were prepared using a soap-less emulsion method. Polymerization was performed in water at a temperature well above the LCST of PNVC so that the monomer segregates into nano/micro-droplets stabilized by the macromonomer polyethylene glycol-mono methacrylate (PEG-MA). Adjusting the polymerization parameters, including usage of different crosslinkers, core-shell nano/micro gels can be prepared changing its diameter from 50 nm to 400 nm, the relative shell size can also be adjusted and the temperature responsive properties maintained. The prepared nano/micro-gels are well-defined nanomaterials for drug delivery applications.

COLL 742

Synthesis of surfactant-free PAA and PMAA nanogels in aqueous media

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In this research, the synthesis of surfactant-free poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) nanogels using hydroxypropylcellulose (HPC) as a template in aqueous HPC solutions around room temperature. Through the hydrogen bonding interaction of acrylic acid (AA) or methacrylic acid (MAA) with hydroxypropylcellulose (HPC), AA or MAA absorbed on the HPC polymer chains and triggered the phase transition of HPC at a lower temperature, with increasing AA and MAA concentration, than the HPC intrinsic phase transition temperature 41 °C. As AA or MAA polymerized to form PAA or PMAA, the much stronger interpolymer hydrogen bonding triggered the phase transition of HPC at a temperature around room temperature, causing HPC coil-global phase transition to collapse and form nanospheres at room temperature, PAA or PMAA hydrogen-bonded HPC chains collapsed and formed nanogels chemically crosslinked by poly(ethylene glycol) diacrylate (PEGDA) or methylenebisacrylamide (BIS). The results showed that all the PAA and PMAA nanogels demonstrated a narrow size distribution. The resulting PAA and PMAA nanogels made with this green synthesis method will promise to find significant applications in pharmaceuticals and personal care.

COLL 743

Osmotic nanospheres – Ideal and switchable dispersants for waterborne dispersions and advanced coatings

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Charged surfactants remain popular dispersants for waterborne dispersions and charge stabilization is very effective. Colloidal stability in such dispersions is sensitive, however, to indifferent electrolyte concentration due to Debye-Hückel screening effects that

decrease inter-particle repulsion potentials. It has been known for some time that osmotic brushes of polymeric electrolytes produce softly repulsive electrosteric stabilization that is insensitive to indifferent electrolyte. Coating particles with such brushes, however, is technically feasible but too expensive in most applications. We have developed osmotic nanospheres that exhibit high adsorption affinity to charged and uncharged particle surfaces and are easily applied in processing that relies upon adsorption from solution. Stimuli-responsive monomers and conventional monomers are used to formulate such nanospheres as lightly crosslinked nanogels. Turbidity studies show that the stability of such nanogels can be maintained at ionic strengths as high as 9 M and switched off at ionic strengths of 0.35 mM using appropriate stimulus-inducing ions. The efficacy of such nanogels is demonstrated by producing concentrated dispersions of hydrophobic carbon including nanotubes, graphene, and hydrothermal carbon as well as model colloids and latexes. Colloidal stability of such dispersions in high electrolyte concentrations is demonstrated and shows immunity to Debye-Hückel charge screening. Stimulus-inducing ions are used to produce controlled dispersion destabilization to produce advanced material coating and deposition. These nanogels are also demonstrated to self-assemble into transparent and mechanically robust thin films. The films are shown to retain the stimuli-responsiveness of the constituent monomers, and to undergo spinodal decomposition to form nano, meso, and microporous open cell porous coatings when exposed to appropriate stimulus-responsive ions.

COLL 744

Layer-by-Layer Functionalized Nanotherapeutics

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Layer-by-Layer assembly is a versatile approach for incorporating a broad range of materials on surfaces based on complementary molecular interactions. As such, LbL offers a high degree of control over the composition of a given material system, with the ability to tune film properties for an array of applications. Using this methodology, we are investigating LbL on nanotherapeutics to impart functionality and to facilitate more efficacious delivery of therapeutics, including synergistic drug combinations. We are also developing a scalable platform for fabrication of these systems in a highly controlled manner by incorporating PRINT nanoparticle technology, presenting exciting opportunities towards reproducibly generating systems that are highly attractive with regard to approval through regulatory pathways as well as industrial manufacture of nanotechnology.

COLL 745

Efficient transdermal penetration of large hydrophilic Bovine Serum Albumin nanodispersions

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Hydrophilic macromolecules such as proteins present extremely low permeability across the skin. This fact is essentially due to the natural physical barrier characteristics of the skin. Furthermore, the permeability of large molecules through intact skin remains a challenging strategy to allow skin absorption of compounds over 500Daltons.

The aim of this work is to develop nanoformulations for transdermal perfusion enhancing their penetration through the skin. For that, a novel oil-based nanodispersion of Albumin with Molecular Weight of 66 KDa was coated with hydrophobic surfactant molecules. The penetration of these Albumin nanodispersions across the skin was validated *in vitro*. The nanodispersion was successfully achieved in transdermal perfusion confirmed by confocal and fluorescent microscopy demonstrating that Albumin-FITC nanodispersion effectively permeated through the pig skin.

The ability to form an oil-based nanodispersion of high MW proteins coated with hydrophobic surfactant molecules enable new strategies to permeate the skin.

COLL 746

Rapidly-dissolvable microneedle patches via a highly scalable and reproducible soft lithography approach

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It has been proven that delivering therapeutics transdermally via microneedle devices can be efficacious while overcoming the extensive side effects of traditional delivery methods. A variety of skin-related diseases could be treated by this modality. To achieve clinical application, microneedles must overcome the elasticity of skin while maintaining controllable shape and composition. Here, we demonstrate the fabrication of highly reproducible and completely dissolvable microneedle patches using a soft lithography process known as PRINT[®] (Particle Replication In Non-wetting Templates). Biocompatible microneedles were made and penetration and dissolution were evaluated by testing patches on *ex vivo* murine and human skin. Epidermal breach was verified by histology and fluorescent drug surrogate was visualized within the skin. Therefore, PRINT microneedles can overcome the epidermis and successfully release drug surrogate, showing their capability to serve as a valuable transdermal delivery method for drug formulations.

COLL 747

Surface modified protein nanocapsules for targeted drug delivery

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For targeted drug delivery it is essential to modify the nanoparticle surface to introduce receptor or ligand molecules rendering them recognizable by the target cells. One advantage of protein particles is that they provide several functional groups on the surface which can be easily used for surface modification.

Here we present different strategies for surface modification of protein nanoparticles. On the one hand simple click-chemistry using chemical cross-linkers was performed to achieve a side specific covalent linkage of folic acid on the particle surface. While in another approach we established a new enzymatic method to produce an antibody-protein conjugate avoiding all kind of toxic chemicals.

Surface modification was monitored by CLSM, LC-MS/MS and SDS-PAGE. Furthermore it was demonstrated that folate based nanocapsules are able to target folate receptor positive macrophages. ELISA and FACS were used to demonstrate the binding ability of conjugated antibody to its antigen.

COLL 748

Monitoring oxidative stress and synthesis of chitosan microspheres for iron overload therapy

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Although iron is essential for many metabolic functions “free iron” participates in the generation of free radicals through Fenton’s Chemistry resulting in the depletion of antioxidants and driving the body into oxidative stress. Oxidative stress is implicated in the pathogenesis many cardiovascular, cancer and neurodegenerative diseases. This study presents novel iron chelators based on coupling iron-chelating moieties onto chitosan microspheres. *In vitro* reaction showed successful coupling of the phenolic molecules as confirmed by HPLC-MS and FTIR. The functionalized chitosan microspheres chelated >70 % as compared to the control. Similarly a method able to monitor the level of oxidants, antioxidants and detect the onset of oxidative stress was developed. This method based on enzymatically generated tetramethoxy azobismethylene quinone (TMAMQ) uses two complimentary approaches. In the presence of antioxidants TMAMQ, a deeply purple quinone is reduced to syringaldazine. Therefore the reduction of TMAMQ or production of syringaldazine can be monitored.

COLL 749

Effects of Diblock Copolymers On Droplet Coalescence, Emulsification, and Aggregation In Immiscible Homopolymer Blends

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Using rheo-optical techniques, we investigated the impact of interfacial wetting of symmetric diblock copolymers (BCPs) on the coalescence and aggregation of polydimethylsiloxane (PDMS) droplets in immiscible polyethylene-propylene (PEP) homopolymers. Anionic polymerization was used to synthesize well-defined matrix homopolymers and PDMS-*b*-PEP diblock copolymers with low polydispersity (PDI ~ 1.02) as characterized with size exclusion chromatography and nuclear magnetic resonance spectroscopy. Blends were formulated to match the viscosities between the droplets and the matrix. Moreover, molecular weights of these components were varied to ensure that the inner block of the copolymer inside the droplet was collapsed and dry, whereas the outer block of the copolymer outside of the droplet was stretched and wet. Droplet breakup and coalescence as well as interfacial surface tensions were measured using rheo-optical experiments with Linkam shearing stage and an optical microscope. Subsequent to droplet breakup at high shear rates, we found that the BCPs mitigated shear-induced coalescence at lower shear rates. Increased BCP stretching was inferred

from surface tension measurements, which indicate that BCP stretching causes the droplet surface to saturate at lower BCP coverages in line with theoretical predictions from wet-dry brush systems. Droplet aggregation was detected with further reductions in shear rate, which was attributed to the dewetting of the matrix from a saturated brush. Ultimately, the regions of droplet coalescence and aggregation were scaled by balancing the forces of shear with those due to the attraction between BCP-coated droplets.

COLL 750

DEVELOPING NEW TECHNOLOGIES FOR ENHANCED OIL REMOVAL USING BENIGN PARTICLES AND BIOMOLECULES

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Removal of surface oil from a spill using magnetic nanocomposites has recently gained a lot of attention. Here, we describe a novel technology for enhancing the removal of surface oil from a spill using an environmentally benign method. We specifically focus on using hydrophobically modified chitosan and magnetic carbon microspheres. The magnetic iron carbon composites are synthesized using a simple aerosol based process using inexpensive precursors such as sucrose and iron sulfate. The iron oxide particles embedded in carbon matrix preferentially remain in the oil phase. The alkyl chains attached to chitosan polymer backbone anchor at the oil water interface allowing the polymer to span the crude oil droplets resulting in a gel-like aggregate. The measurement of dynamic modulus of the oil phase shows shear thinning gel-like characteristics. This gel-like phase of crude oil droplets containing magnetic carbon spheres can be removed as an aggregate using a strong magnet resulting in enhanced recovery of crude oil.

COLL 751

Active Alcoholic Solutions and Silane-in-Water Emulsions for the Formation of Siloxane Based Films from Hydrosilane/Alkoxysilane Condensation

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Sol-gel processes, both acid- or base-catalyzed, are the traditional and efficient way to prepare siloxane-based elastomers and coating of a variety of types. However, controlling the kinetics of the process and managing shelf life, which is affected by

humidity, is challenging. The condensation of hydro- with alkoxy silanes catalyzed by $B(C_6F_5)_3$ provides an alternative route to highly reticulated siloxane films that is less susceptible to humidity. Combinations of tetraalkoxysilane and tetrahydrosiloxanes could be formulated in various alcohols to give solutions that are stable over months. After coating substrates, however, the catalyst is activated and leads to rapid formation of films or, at will, foamed structures. By contrast, when formulated in water, emulsions form with droplets that are stable over weeks. The conversion to films by coating substrates and drying leads to fused particle films of high porosity. The ability to control film structure in the two cases will be discussed.

COLL 752

Effect of composition and formulation variables in biomass flooding capacity by o/w microemulsions

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The relation between microemulsion formulation and the ability to effectively penetrate the complex capillary structure of wood is discussed. We have proven that biomass impregnation via complex fluids enhances fluid penetration in, e.g., wood (JCIS 381, 171–179, 2012); however, there still was uncertainty about the role of emulsion formulation. In this investigation we developed microemulsions with different compositions and physical-chemical formulations and the extent of their penetration in different wood species was evaluated. Oil concentration and the salinity of the aqueous phase critically affected the extent of the penetration. In general, compositions leading to high viscous systems were less effective for wood impregnation. In addition, surfactant choice and the synergies in surfactants mixtures played an important role as far as the extent and dynamics of fluid penetration. This is explained by the affinity between the surfactant(s) and the solid which contains conductive elements with different biomolecular constituents. With the appropriate surfactant mixture it was possible to enhance the penetration of the microemulsions in white pine from 15 to 83%, compared to water at atmospheric pressure and room temperature. Overall, the physical and chemical characteristics of the wood specie are shown to have a critical influence in the extent of penetration

COLL 753

New anionic-nonionic double-tail surfactant for high-temperature and low-salinity reservoirs

Impact of the surface rheology on the kinetics of Ostwald ripening of foams stabilized with saponins

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Saponins are a class of natural surfactants found in more than 500 plant species. They consist of flat hydrophobic head group (triterpenoid or steroid) with hydrophilic polysaccharide chains. In previous articles [1, 2, 3] we studied the surface rheological behavior of saponin adsorption layers, subjected to steady or oscillatory deformation in dilatation or shear. Generally triterpenoids exhibited high modulus both in dilatation (E) and in shear (G) deformation, while steroids had moderate modulus in dilatation, and negligible modulus in shear. The surface properties of saponins make them very good foam stabilizers. In this work we study the kinetics of Ostwald ripening (OR) of saponin-stabilized foams. We use various saponins, with well-characterized surface rheological properties. The change of the bubble size over time was measured. Then we followed a procedure described in [4] to calculate the gas permittivity, k , of the adsorption layer from the evolution of the bubble size distribution. Triterpenoids inhibited significantly the rate of OR. Steroids also had an inhibitory effect, but it was much less pronounced. No clear correlation was established between the rate of OR and the surface modulus in particular mode (shear or dilatational). The impact of other surface properties and phenomena on the rate of OR is discussed: (1) Magnitude of $E+G$; (2) Surface stress; (3) Hysteresis during expansion/compression cycle of the surface.

COLL 755

Evaporative destabilization of double emulsions for effective triggering of release

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Double-emulsion formulations have a compartmentalized structure that can provide high capacity of entrapment, protection of fragile substances, combination of incompatible substances in one product, and controlled release. We successfully prepared volatile water-in-oil-in-water ($W_1/O/W_2$) double emulsions with a cream-like texture for potential application in dermal delivery. This was achieved by selecting skin-compatible and volatile cyclomethicones, as the oil phase (O) of $W_1/O/W_2$ double emulsions. Several surfactants (Abil[®] EM90, Abil[®] Care 85, and Tween 80) were used to stabilize the double emulsion structure and TEGO[®] Carbomer 341 ER thickener was added to reach a viscosity ratio that allowed optimal formation of double-emulsion globules.

The double-emulsion's evaporation behavior was studied by use of thermogravimetric analysis (TGA) in order to understand the release mechanism of the internal aqueous phase (W_1). The evaporation rates for the different double emulsions were compared

against a mathematical model system, in which all three phases were expected to evaporate simultaneously, independently, and at constant rate. Some similar characteristics between the model and the experimental data such as total evaporation time and presence of different evaporation stages were found. Finally, protein release studies at skin-like thermal conditions were carried out. It was found that the evaporation of $W_1/O/W_2$ double emulsions may act as an effective trigger mechanism for the release of ingredients in the W_1 phase. The release rate of the contents can be tuned by composition design, that is, by selecting oils with the appropriate volatility; the higher the volatility of the oil the faster the release rate of the internal aqueous phase.

The understanding of the evaporation mechanism exhibited in volatile double-emulsion formulations is important for the controlled release of active substances involving applications of interest for cosmetic or pharmaceutical industries.

COLL 756

Effects of Water Volume on Interfacial Dynamic Behaviors between Clathrate Hydrates and Water

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This work investigated the effect of water volume on the interfacial dynamic behavior between cyclopentane (CP) hydrates and water droplet in a CP/n-decane oil mixture. The interfacial force between CP hydrates and water droplet was identified by using the z-directional microbalance. Repetition of precise measurements over several cycles from contact to detachment is obtained from 100 to 600 μL of water droplet. It is confirmed that as the volume of water droplet increases, the contact force between CP hydrates and water also increases up to 300 μL . In addition, there is no significant change of contact force over 300 μL of water droplet. We also identified the effect of surfactant solutions including sodium-dodecyl sulfate (SDS) and dodecyl-trimethylammonium bromide (DTAB) on the interfacial force. These results provide useful information and new insights for understanding complex behavior of hydrate particles on the consideration of flow assurance approaches.

COLL 757

Mechanism of double phase separation of aqueous two-phase copolymerization of acrylamide and quaternary ammonium cationic monomers

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In the aqueous two-phase copolymerization of acrylamide and 2-methylacryloylxyethyl trimethyl ammonium chloride (DMC), double phase separation was first observed. To fix

the critical points, spectrophotometer was employed to detect the transmittance of copolymerization system on-line. The transmittance curves showed three intervals. At 1st interval, transmittance keeps constant at the beginning, and then drops off quickly. At 2nd interval, transmittance stops dropping and begins to increase. And at 3rd interval, transmittance stops to keep constant for a moment, and then drops rapidly to nearly zero. When acrylamide was copolymerized with different monomers, the double phase separation process can be observed only for DMC and acryloylxyethyl trimethyl ammonium chloride (DAC). It confirms that the double phase separation is attributed to the cationic nature of DMC and DAC. And then after a series of valid experiments, mechanism of the double phase separation process of the aqueous two-phase copolymerization system was brought up.

COLL 758

Fundamental property and Functional Aptitude Relationships in Emulsion and Foam Applications of Amphiphilic Compounds

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Amphiphilic compounds are issued of a combination of two opposite entities, covalently assembled within a single structure. By the diversity of the origin, class, number of monomer and substitute, size, linker or spacer, stereochemistry of the molecular entities, their chemical structure may be very different but also close each other. However, they may fulfill the same role in reducing surface and interfacial free energy in dynamic or static ways, ensuring especially the formation of dispersed systems like emulsion and foam. If the relationships between the structural variable and fundamental properties are strictly chemical residue dependent, those between fundamental and functional aptitudes are not necessarily. In this case, general and universal rules may exist, whatever the kind of amphiphilic compounds. In order to achieve a rational design for any expected functionality, we attempt to find out some predictive and conception rules from a lot of screening data of fundamental and functional properties. In this communication, some correlations between fundamental data related to surface and interfacial properties, measured by molecule adsorption or spreading under dynamic or static mode, in compression or dilation of adsorbed or spread film, and emulsifying and foaming performances of various bio-based surfactants will be presented.

COLL 759

DNA directed multi-enzyme co-localization on nanoparticles

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Widely existing multi-enzyme complexes (MECs) in nature exhibit highly efficient catalytic mechanism in cascaded reactions, which has inspired researchers to develop novel strategies to mimic MEC structure and function *in vitro*. It has been found that the spatial arrangement and orientation of multiple enzymes in artificial MECs plays a significant role in facilitating cooperative enzymatic activity. DNA hybridization provides unique effective control of the relative positions of different enzymes in multi-enzyme co-localization. It is also known that, compared to planar surfaces, a spherical geometry is more suitable for co-localization of multiple layers of enzymes due to lesser steric hindrance. To demonstrate this concept, glucose oxidase (GOX) and horseradish peroxidase (HRP) were co-localized onto polystyrene nanoparticles via specific DNA hybridization. In comparison with planar polystyrene films, it was shown that the nanoparticles provided higher hybridization efficiency. This behavior was also shown to be a function of particle size. Various capture DNA concentrations were compared and optimized. The co-localization of GOX and HRP were evidenced by FRET studies of the dyes labeling the two enzymes. In addition, different molar ratios of multiple enzymes in DNA directed co-localization were investigated. In summary, DNA directed co-localization of enzymes provides precise control over the relative positions of the enzymes to mimic MECs.

COLL 760

Self assembled systems the conservation of cultural heritage

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New perspectives have been opened by the application of self-assembled systems to Conservation, generating a breakthrough in the development of innovative tools for the conservation and preservation of cultural heritage. This contribution is an overview of the most recent methodologies developed in the Conservation field, focusing on amphiphilic systems, and gels. We report on the characterization of two systems, EAPC and XYL, which have shown good to optimal performances in the removal of organic polymers from wall paintings. EAPC is a five-components fluid composed of water, sodium dodecylsulfate (SDS), 1-pentanol (PeOH), propylene carbonate (PC), and ethyl acetate (EA), while XYL is a "classical" o/w microemulsion where p-xylene droplets are stabilized in water by SDS and PeOH. Small-angle neutron scattering (SANS) with contrast variation is used to infer a detailed picture of the structure of these complex fluids. We found that the composition and the structure at the nanoscale determine the capability of removing a broad range of different polymer coatings from porous materials.

@No kinship exists among authors

COLL 761

Enzymatic decontamination of organophosphate agents: From enzyme-polymer conjugate to micelle self-assembly

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The use of enzyme based decontamination has attracted a lot of attention due to its potential use in the non-toxic and non-corrosive decontamination of chemical warfare agents (CWAs). We describe a novel decontamination formulation based on a conjugate of block-copolymer with enzymes such as bovine serum albumin (BSA) that are capable of binding and degrading various organophosphate pesticides. Pluronic block-copolymers were employed to increase the solubility of the CWAs. The BSA was first chemically conjugated to Pluronic, and the BSA-Pluronic conjugate spontaneously self-assembles into micelles with a controllable size. The hydrolytic activity of organophosphate agents by the micelles was determined using paraoxon as a substrate, and the results show that the micelles have a higher enzymatic activity than that of the free BSA. We hypothesize that micelles increase the solubility of the CWAs by sequestering them into micelles and enhance the localization of the BSA, allowing a better enzyme-substrate interaction.

COLL 762

Emulsification of Aqueous-Based Liquid Crystals by Single-Chain Surfactants and Effect of Odd-Even Parity of Alkyl-Chain on Droplet Formation

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Single-chain surfactants usually emulsify oily substances in water. Here, we report a co-assembly system in which generic single-chain anionic or nonionic surfactants emulsify a class of water-soluble, nonamphiphilic organic salts in water. The encapsulation of the hydrated threads of nonamphiphilic organic salts by surfactants promotes formation of chromonic liquid crystal droplets with tactoidal and radial shapes. The odd-even parity of alkyl chain length also oscillates the ability of the single-chain surfactant to emulsify the nonamphiphilic molecules in the water-based liquid crystal droplets. Confocal fluorescence microscopy with 0.002 wt% of fluorescently tagged surfactant and TEM microscopy using negative staining supported a bilayer coating of the single-chain surfactants on the droplets, consistent with the formation of giant vesicles. The molecular assembly in the liquid crystal droplets was characterized by cryoTEM. These

new self-assemblies have the potential for fabrication of new soft organic microcapsules.

COLL 763

Efficient synthesis of amine-functional diblock copolymer nanoparticles via RAFT dispersion polymerization of benzyl methacrylate in alcoholic media

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Benzyl methacrylate (BzMA) is polymerised via reversible addition-fragmentation chain transfer (RAFT) chemistry under alcoholic dispersion polymerization conditions in ethanol using a poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent (CTA) at 70°C. Polymerization-induced self-assembly (PISA) can lead to formation of either spherical micelles, worm-like micelles or vesicles. The preferred morphology depends on the molecular curvature of the PDMA-PBzMA diblock copolymer chains. ¹H NMR confirms that high monomer conversions are achieved within 24 h (>99%), THF GPC analyses indicate relatively low polydispersities ($M_w/M_n < 1.30$) for the diblock copolymers, suggesting good pseudo-living character. When transferred from ethanol to water, the nanoparticles remain colloidally stable and acquire appreciable cationic character, as judged by DLS and aqueous electrophoresis studies, respectively. Using a relatively long PDMA CTA allows near-monodisperse spherical micelles with tunable diameters from 30 to 100 nm to be prepared simply by varying the target degree of polymerization of the core-forming PBzMA block.

COLL 764

Unraveling the origin of the viscosity peak in micellar solutions by cryo-TEM

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Our filed has established profound understanding of most of the key aspects of micellization. An exception is the origin of the viscosity peak in micellar solutions discovered by Prof. Hoffmann more than 2 decades ago, which remains a puzzling phenomenon to-date. That pioneering work and following studies in charged and uncharged systems reported that the zero-shear viscosity can become a million times greater than the solvent viscosity, and display one or two maxima. The growths rules responsible for the first viscosity decrease are not resolved, and there is no clear explanation for the existence of a second maximum region. Using cryo-TEM we revealed a number of growth mechanisms and structures along the first peak, and for the first time resolved the nanostructures associated with the second viscosity peak. Moreover, we established a clear understanding of micellar growth laws affecting the viscosity, and the relations between the chemical structure, the micelles nanostructure,

and the solution viscosity. This understanding allows us to predict the formation of a viscosity peak and the mechanism associated with the viscosity decrease, for some given compositions.

COLL 765

Light scattering maxima near micellar CMC and relationship to target molecule loading capacity and release

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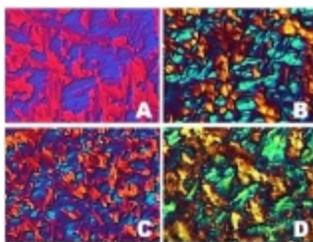
A sharp maximum in light scattering occurs in many surfactant solutions when they are diluted through their critical micelle concentration (CMC). This effect has historically been linked to impurities in the micellar solutions. Monitoring of the scattering and intrinsic viscosity behavior of sodium dodecyl sulfate (SDS) micelles under a gradient dilution when they are deliberately loaded with an impurity (dodecanol) allows unusual features of the scattering maximum to be explored and linked back to micelle behavior. The concentration at which the onset of the maximum occurs, its width, and the scattering amplitude are directly related to the ratio of impurity to surfactant and further correlated with the loading capacity of the micelles. The data suggest that the release of dodecanol nanoparticles as the CMC is approached is responsible for the scattering behavior. The ionic strength of the aqueous solution has extremely strong effects on all the features of the scattering maximum and its relationship to impurity loading capacity and release. A model for these experimental characteristics is presented in this work.

COLL 766

Characterization of the thermotropic properties of novel catanionic surfactants existing as room-temperature liquid crystals

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A series of catanionic surfactants were synthesized from single- and double-chain quaternary- ammonium surfactants as the cationic counterpart and bis-(2-ethylhexyl)sulfosuccinate as the anionic counterpart by ion-exchange metathesis reaction involving the corresponding quaternary ammonium surfactant and the sodium salt of the anionic surfactant. Their thermal as well as liquid crystalline properties were studied by Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Hot-Stage Polarized Light Microscopy (HSPLM), and X-ray Diffraction (XRD). They exist as room-temperature liquid crystals.



COLL 767

Salt bridging of surfactant template in the synthesis of submicrometer hollow particles

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Hollow particles are promising for various applications in catalysis, rechargeable batteries, gas sensors, drug delivery systems and biomedical imaging agents. The structural transition from ordered mesoporous to hollow particles is possible by exploiting surfactant self-assembly and preferential partitioning between different species in the precursor solution. In our previous work, the synthesis of submicrometer hollow silica particles encapsulating ferromagnetic iron oxide using the aerosol-based

process has been described. The objective here is to investigate the colloidal interactions that produce these hollow particles through the aerosol-based process. We hypothesize that the structural transition results from the disruption of the co-assembly of silicate and surfactant (CTAB), by the preferential partitioning of surfactant to FeCl_3 by salt bridges. The salt bridging effect in the precursor solution will be characterized by light scattering, NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). This knowledge is essential in designing materials for various applications.

COLL 768

The Growing Importance of Reverse Micelles in Understanding Industrial Metals Separations

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70 years of research into solvent extraction – a hugely important industrial metals separations method – has traditionally been understood in terms of metal ion coordination chemistry. More recently, however, reverse micelles (RMs) have been found to play a significant role in the separation properties of solvent extraction systems. We explore the effect of RMs on metal separations, presenting both current understanding and new results that suggest that these aggregates are pivotal in defining the physical behavior of solvent extraction systems. Understanding solvent extraction in terms of micelles joins two mature fields of science to yield fresh insight into the fundamental mechanisms driving industrial separations. Realizing control of the nano-scale micellar behavior in solvent extraction systems through fundamental research may result in significant improvements to commercial separations processes including nuclear fuel reprocessing as well as precious, rare earth and base metal production.

COLL 769

Diamond-based "smart" electrodes for electro- and photocatalysis

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One of the key challenges in renewable energy is the development of robust, selective electrocatalytic interfaces. Recently, diamond has emerged as an ideal platform for hybrid electrodes because of diamond's extreme stability over a wide range of pH and electrochemical potentials. Diamond thin films and doped polycrystalline substrates are inexpensive and provide unprecedented stability. By covalently linking molecular catalysts such as coordination complexes and/or porphyrins to diamond electrodes using "click" chemistry, we are aiming to make "smart" electrodes that combine the

stability and ease of handling of diamond with the selectivity of molecular catalysts. One key issue has been understanding how electron transfer rates of surface-tethered redox complexes are affected by the molecule-surface linkage, where we observe results quite different from those of traditional self-assembled monolayers. Using this approach we have made surface-tethered Ru coordination complexes with excellent electrochemical behavior even at high potentials, and also surface-tethered porphyrins able to reduce CO₂ to CO. Finally, we are also exploring a completely new approach to photocatalysis, using diamond electrodes as a direct solid-state electron emitter to enable very difficult electrochemical reduction reactions beyond the limits of existing molecular catalysts.

COLL 770

Electrochemical conversion of CO₂ to organic products in an aromatic amine catalyzed environment

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We have proposed the electrosynthesis of alcohols from CO₂ as an energy conversion and storage approach, which recycles atmospheric carbon. However, the large activation energy associated with this multielectron, multiproton reduction makes conversion of CO₂ problematic. Electrochemical and photoelectrochemical schemes for this conversion only become possible if the system activation overpotentials can be lowered to ~200-400mV. To this end, we have discovered that aqueous aromatic amines such as pyridinium or imidazolium are efficient catalysts for the reduction of CO₂ at a variety of metal and semiconductor cathodes. At an illuminated p-GaP cathode, we find that faradaic efficiencies can be >95%, for methanol production when run at 200mV of underpotential. At platinized p-GaAs photocathodes carbon-carbon coupling is observed to dominate producing isopropanol and acetone as the major products when pyridinium is utilized as the electrocatalyst. The observed reduction involves a mediated charge transfer process, which is initiated by the one electron reduction of the aromatic amine. We hypothesize this transformation occurs through the formation and reduction of a carbamate intermediate.

COLL 771

Si nanowires-based carbon dioxide fixation with highly specific organic products

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Natural photosynthesis harvests the energy in visible light to power chemical reactions and uses CO₂ as the carbon source. Because light as an energy source

is free and abundant, chemical reactions similar to photosynthesis have major fundamental and practical implications. Indeed, significant efforts have been attracted to this research goal. The majority of attention for photochemical reactions that transform CO₂ have focused primarily on conversion into *fuels*. How to learn from photosynthesis and devise reaction routes for the synthesis of useful organic compounds receives relatively underwhelmed considerations. Drawing inspiration from the mechanisms found in dark reactions of photosynthesis and using p-type Si nanowires as a photocathode, here we show that highly specific reactions can be readily carried out to produce α-hydroxy acids by photoreduction of aromatic ketones, followed by CO₂ fixation. Powered by visible light, this reaction is in close resemblance to natural photosynthesis, and different from its electrochemical analogues. The carboxylation products of two of the substrates examined in this communication serve as precursors to nonsteroidal anti inflammatory drugs (NSAID), ibuprofen and naproxen.

COLL 772

Electrochemical CO₂ reduction catalyzed by oxide-derived metal nanoparticles

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Metal nanoparticles prepared by reducing bulk metal oxide precursors are energetically efficient and robust catalysts for the electrochemical reduction of CO₂ to CO and other simple carbon feedstocks. This talk will describe the physical properties and catalytic activities of the “oxide-derived nanoparticles” of Cu, Au, Ag and Pd. We will present evidence that the oxide reduction process kinetically traps metastable surface structures on the nanoparticles that are responsible for their exceptional CO₂ reduction activities. In addition, the catalysts' resistance to deactivation has enabled the measurement of electrokinetic parameters that illuminate mechanistic features of their CO₂ reduction pathways. Metal oxide reduction represents a “top-down” approach to metal nanoparticle synthesis that may provide access to unique surface structures for both electrochemical and non-electrochemical catalysis.

COLL 773

Highly efficient mononuclear iridium complex photocatalyst for CO₂ reduction under visible light

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We have successfully developed mononuclear Ir complex photocatalysts for efficient and selective CO₂ reduction to CO, which are driven by visible light in a homogeneous

solution even in the H₂O mixed solution. The most efficient Ir complex photocatalyst showed TN_{CO} value of 50 and the quantum yield Φ_{CO} of 0.21, which is the best reported value in homogeneous photocatalytic systems using visible light at wavelengths such as 480 nm. The reaction mechanism of efficient photocatalytic CO₂ reduction using the Ir complex was determined using ¹H-NMR, ESI-MS, and absorption change spectra. The Ir complex was transformed into iridium-hydride complex during the photocatalytic reaction, *i.e.*, iridium-hydride complex is the active photocatalyst. As for the reaction mechanism, it is speculated that one-electron-reduced species of iridium-hydride complex can react with CO₂ and that iridium-hydride complex probably donates electrons to the CO₂ adduct.

COLL 774

Photonanomaterials for CO₂ reduction to methanol

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CO₂ can be converted into methanol, through the intermediate steps of reduction to formic acid and formaldehyde using a triad of enzymes such as formate dehydrogenase (FatoDH), formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH).

In each reductive step one mole of NADH is oxidized to NAD⁺ that has to be converted back to NADH in order to make the process acceptable from an economic point of view. Such regeneration can be accomplished by chemical, electrochemical, photochemical or photoelectrochemical processes.

Recent studies have shown that the photosystems can be integrated with enzymes and give interesting results. Different semiconducting materials have been prepared: transition metals sulphides and nonstoichiometric mixed sulphides, materials modified with metal cocatalysts, composites of metal oxides like Cu₂O/TiO₂ and the other like vanadate *ect.*

Here, we describe the behaviour of some semiconductors and show that they are interesting agents for the reduction of NAD⁺ and the regeneration of NADH.

COLL 775

Multielectron Oxidation of Water Mediated by Mn Oxides: Mechanism and Visible-light Sensitization for Artificial Photosynthesis

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The water oxidation reaction occurs at the extraordinary high catalytic activity in the naturally occurring photosynthetic Mn centre. However, synthetic manganese compounds are quite inefficient for this oxidation reaction and it hampers the utilization of inexpensive and abundant Mn oxides as a component for artificial photosynthesis. In this presentation, based on the recent finding that surface-associated Mn(III) serves as the rate-determining intermediate species for electrooxidation of water by Mn oxides, the author discusses the plausible origin of the remarkable difference in catalytic activity between the photosynthetic and the synthetic Mn catalysts. The author also discusses the way to couple O₂-evolving Mn-oxide catalysts to CO₂ reducing units to accomplish fuel production under visible light irradiation.

COLL 776

Tip-Enhanced Raman Spectroscopy Investigation of the Adsorption of Osteopontin to Calcium Oxalate Monohydrate Crystals.

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Tip enhanced Raman Spectroscopy (TERS) is a sensitive surface specific technique that combines the spatial resolution of scanning probe microscopy with the chemical specificity of Raman microspectroscopy. The TERS tip performs as a nanoscale antenna of ~20 nm diameter that scans the object enhancing the Raman signal from the optical near-field region of the sample. In this study, TERS was used to investigate the adsorption of the phosphoprotein osteopontin onto the surface of a calcium oxalate monohydrate microcrystals that are the major constituents of kidney stones. Osteopontin is known to be an efficient inhibitor of COM formation and knowledge about its interaction and adsorption to distinct facets of the crystal are relevant to prevent the formation of such stones. Raman maps along with the observed variation of the relative peak intensities of the TERS spectra were collected to probe the distribution of the phosphoprotein adsorbed to the crystal.

COLL 777

Strategies for highly-ordered and thermally robust organic layers at metal surfaces

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The use of small organic molecules to control surface structure as well as electronic and chemical functionality is a critical field for the development of inexpensive and highly functional organic technologies in energy conversion, sensors, electronics, and other applications. We study the self-assembly of highly-ordered organic nanostructures at

surfaces to develop well-controlled, functional organic layers. Characterization is made by high-resolution scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy, and high-resolution electron energy loss spectroscopy. Here we report on progress using carboxylic acid functional groups both in direct bonding to the Cu(100) surface as well as in highly-robust, self-assembled ionically bonded architectures. The latter form by an on-surface reaction with NaCl, show uniform ordering with annealing, and have high thermal stability, as determined by molecular resolution STM at high temperatures. Interfacial organic layers are also studied to enable highly-ordered structures from molecules that do not order directly on the metal surface.

COLL 778

Inversion of the electric field at the electrified liquid-liquid interface

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The thermodynamics of the general system of two immiscible electrolytes in the presence of an electric field depends strongly on the distribution of ions near the liquid interface. Here, we calculate the corresponding electrostatic potential difference, excess surface tension, and differential capacity via Monte Carlo simulations, which include ion correlations and polarization effects, and via a modified non-linear Poisson-Boltzmann theory. Macroscopically, we find good agreement between our results and experimental data without needing any fitting parameter. At higher salt concentrations, charge overcompensation in the lower-permittivity region is observed, which results in a local inversion of the electric field accompanied by charge inversion near the interface. We find that these interesting phenomena are mainly driven by the excluded-volume effects associated with large organic ions in the oil phase, although polarization effects and between-layer ion correlations have a significant impact in the adsorption of ions close to the liquid interface. In addition, our Monte Carlo simulations predict that the differential capacity is maximal at the point of zero charge, in contrast with the classical Poisson-Boltzmann theory results.

COLL 779

Sacrificial bonds created with polyelectrolyte and nanoparticles

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Adhesion of dry and wet surfaces treated with polyelectrolyte complexes (PECs) or multilayers (PEMs) of PAH/PAA or CPAM/silica nanoparticles (PPECs or PPEMs) were studied using AFM adhesion measurements. The aim was to introduce sacrificial bonds similar to those found in human bones between these surfaces. In dry state PEMs gave

higher adhesion than PECs for the PAH/PAA system, but adhesion did not differ significantly between PPEMs and PPECs for the CPAM/nano particle system. However, the latter system displayed a multiple-release pattern characteristic for sacrificial bonds. The results in wet state showed the expected long-range disentanglement with PPECs but the pull-off forces were generally low. Treatment with PPEMs produced higher pull-off values, together with disentanglement behavior, possibly due to better contact between the surfaces. PECs made from PAH/PAA showed significantly higher pull-off values compared to the PPECs, probably due to polymer interdiffusion across the surface boundary.

COLL 780

Adsorption energetics and reactions of ethylene carbonate-lithium and reaction pathways on C(0001)

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The decomposition of molecular electrolytes at carbon anode surfaces in Li-ion energy storage devices creates a passivating layer known as the solid electrolyte interphase (SEI). The energetics and molecular events in the formation of the SEI layer are not yet firmly established. To investigate the onset of SEI formation, a Li-HOPG(C(0001))-ethylene carbonate(EC) model system was created under ultra-high vacuum(UHV). The impact of Li^+ on the binding of EC towards the C(0001) surface was studied quantitatively. Temperature programmed desorption (TPD) spectra showed that the 0.78 ± 0.06 eV EC binding energy on neat HOPG increases to 1.19 ± 0.10 eV upon lithiation. At higher lithium loadings, temperature programmed reaction spectroscopy (TPRS) was used to track Li-metal induced EC decomposition. Condensation reactions involving Li^+EC^- radicals were followed via C_2H_4 elimination. Branching between different reaction pathways was determined through CO_2 fragment yields from decomposition products. We compare thermal pathways and branching to electrochemical pathways reported in the literature.

COLL 781

Formation and characterization of redox active molecules on semiconductor surfaces

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The incorporation of redox active molecules on semiconductor surfaces is important from a number of applications such as molecular electronics, sensors, and biological and energy-related applications. This presentation will address formation and

characterization of molecular layers on silicon via two routes. The first route involves the formation of aliphatic monolayers on silicon and the inclusion of redox active ions on the terminal carboxylate group. The second route involves a click chemistry approach to incorporate larger redox active organometallic species to the silicon surface. In both cases, the monolayers were characterized with spectroscopic ellipsometry, contact angle, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. In addition, the electrical properties of these monolayers were characterized by forming metal-molecule-silicon junctions by using multiple soft metallization techniques, which include flip chip lamination and an indium gallium eutectic.

COLL 782

Designing and Imaging Isolated Bimolecular Stereospecific Structures on a Platinum Surface

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The stereocontrol of chemical reactions on surfaces is one of the most challenging tasks in developing new generations of highly selective heterogeneous asymmetric catalysts. STM imaging coupled with DFT calculations provides a uniquely powerful method for addressing the current lack of a detailed molecular understanding of catalytic asymmetric induction on surfaces. In combination, these techniques can be used to observe and define transient chemisorbed pre-organization complexes operating the chirality transfer. We present sub-molecularly resolved regiospecific and stereospecific data for isolated bimolecular and termolecular assemblies formed between chiral and prochiral molecules on a platinum surface. The studies were performed using a combination of variable temperature STM imaging, DFT calculations, catalytic tests, and organic chemistry approaches. The results show how site-specific chemisorption can cooperate with multiple non-covalent bonding in the formation of stereodirecting complexes. They also show how surface analysis at the molecular scale can be bridged to organic chemistry problems.

COLL 783

Linking interfacial chemistry of CO₂ to surface structures of hydrated metal oxide nanoparticles

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The surface properties of metal oxide nanoparticles (NPs) are critical for their performance as (photo)catalysts and adsorbents. However, characterization of the

microscopic (related to specific adsorption sites) surface and acid-base properties of the hydrated NPs is an extremely challenging task. This study demonstrates the capabilities of molecular probe FTIR spectroscopy combined with H/D solvent isotope effect and using atmospheric CO₂ as a probe in *in situ* characterizing surfaces of hydrated metal (hydr)oxide NPs. Using this approach, we show that rhombohedral hematite NPs synthesized by forced hydrolysis are enclosed by stoichiometric {104} facets, while ferrihydrite-like surface defects are stabilized in the roughened rounded areas of the acute edges of the NP facets. These results confirm that the nanosize-induced phase transformation of hematite is directed toward ferrihydrite, the process starting from the crystal edges. We also apply this method to understand the effects of acidic and alkaline etching on the surface structures of hematite NPs. The established structure-property relationships for the carbonate adsorption can be used for non-invasive and fast characterization of the surface properties of corundum-type sesquioxide NPs.

COLL 784

Competing reactions on monolayers: Formation of amide linkages via succinimidyl ester chemistry

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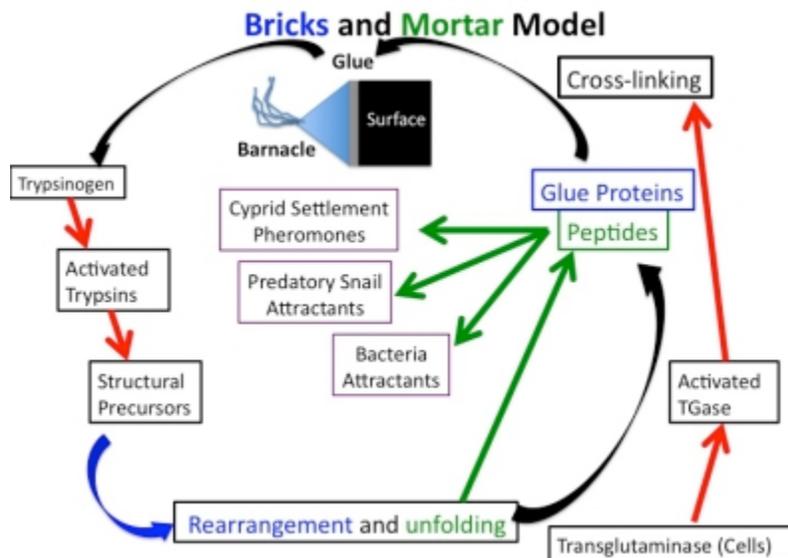
Monolayers with *N*-hydroxysuccinimide (NHS) ester terminal groups are widely used to couple amine-containing biomolecules such as proteins and peptides to surfaces for many types of bioanalytical platforms. Though this pathway simplifies tethering of biomolecules to surfaces via amide linkages, hydrolysis of the NHS group competes with amidization. This presentation discusses an investigation using succinimidyl ester-terminated monolayers on gold formed from disulfides of various chain lengths. Hydrolysis reactions were performed in borate buffer, while aminolysis reactions used a model amine molecule at various concentrations (50 to 500 mM) and pH (8.5 to 10.5). Structure and reactivity of these adlayers were analyzed using infrared reflection spectroscopy, X-ray photoelectron spectroscopy, electrochemical reductive desorption, and contact angle measurements. Results show hydrolysis occurs more rapidly for shorter chain length systems, but aminolysis overcomes hydrolysis at higher amine concentrations and pH. The importance of applying this form of coupling chemistry to protein immobilization is discussed.

COLL 785

Glues, structural proteins, enzymes and siloxanes: Molecular stews and stewardship

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Future fouling management will be surfaces that can be cleaned. Biological glues are central to effective cleaning strategies. Most biological glues adhere poorly to siloxanes. I will talk about how some biological glues cure and the roles of enzymes and peptides



. I will then discuss the roles of these same peptides as biological signals and the impacts of components of polysiloxanes on enzymes implicated in glue curing. These examples provide perspective on potential environmental impacts of organosilicons.

COLL 786

Exploring the mechanisms underlying why temperature affects the adhesive tenacity of barnacles grown on non-toxic marine coatings

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Barnacles are often the dominant hard foulers in marine waters, attaching to substrates by secreting a proteinaceous adhesive. Previous experiments in our lab have shown an inverse relationship between critical removal stress (CRS) and the temperature at which

barnacles were reared. The mechanism accounting for the temperature effect is still unknown and could be mediated through changes to the composition and amount of the adhesive. To investigate the underlying mechanism responsible for the temperature effect we are using a combination of 2D-E proteomics, direct observations of growth ring and cementing systems, and by conducting FTIR microscopy to confirm chemical differences between cement secreted at different temperatures. Our working hypothesis is that the temperature at which animals grow may affect the density of the cementing system and thus the composition and abundance of adhesive proteins.

COLL 787

Fouling deterrence, an effective strategy to eliminate marine invertebrate biofouling

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Fouling deterrence is a promising antifouling strategy which prevents marine invertebrate biofouling via pharmacokinetic interruption of adrenergic receptor mediated neurological sensing mechanisms in larval marine invertebrate such as barnacle cyprids and oyster pediveligers. Adrenergic receptors have been identified as being one of the important receptor groups mediating settlement in larval invertebrates. At a molecular level, recent oyster genomic studies and immunocytochemical investigations from our lab have revealed that there is a dedicated family of adrenergic receptors that are the likely participants of the settling response. Our comparative investigations have also revealed that other problematic marine invertebrate biofoulers such as the encrusting bryozoans as well as other mollusks including Zebra Mussels and the Asiatic Clam may be effectively deterred from settling on treated surfaces coated with adrenergic ligands. Perhaps the most promising highly effective antifouling coatings will be multi-modal, incorporating both passive antifouling surface chemistries and relevant biologically active fouling deterrent moieties to act over a wide range of spatial and temporal scales.

COLL 788

Elucidating the organismal and biomolecular composition of ship hull biofouling communities

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The advent of culture-independent molecular biological measurements have aided in overcoming some of the limitations associated with our inability to culture the vast majority of microbial species and as such, have become powerful tools for understanding the composition, potential and function of marine biofilm and biofouling communities. In this study, we combined the use of large-scale genetic and proteomic measurements with traditional biochemical analyses to begin to understand the role differing environments play in determining the composition of air-water interface biofouling communities that were sampled from the hulls of U.S. Navy vessels deployed in different geographic waters. Despite being harvested from identical substrates, our findings (i) highlight qualitative and quantitative differences in the organismal and biomolecular profiles of these biofouling communities, (ii) provide a baseline understanding for comparative analyses and (iii) identify caveats in the interpretation of stand-alone molecular biological datasets when attempting to characterize highly complex microbial assemblages.

COLL 789

Thiol-stabilized, plasmonic gold-silver nanoalloy clusters

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Atomically precise thiolate-stabilized gold nanoclusters are currently of interest for many cross-disciplinary applications in chemistry, physics, and molecular biology. Very recently, synthesis and electronic properties of "nanoalloy" clusters $\text{Au}_{144-x}\text{Ag}_x(\text{SR})_{60}$ were reported. Here density functional theory is used for electronic structure and bonding in $\text{Au}_{144-x}\text{Ag}_x(\text{SR})_{60}$ based on a structural model of the icosahedral $\text{Au}_{144}(\text{SR})_{60}$ that features a 114-atom metal core with 60 symmetry-equivalent surface sites and a protecting layer of 30 RSAuSR units. In the optimal configuration the 60 surface sites of the core are occupied by silver in $\text{Au}_{84}\text{Ag}_{60}(\text{SR})_{60}$. Silver enhances the electron shell structure around the Fermi level in the metal core, which is reflected in the electronic metal-to-metal transitions. The calculations also imply element-dependent absorption edges for $\text{Au}(5d) \rightarrow \text{Au}(6sp)$ and $\text{Ag}(4d) \rightarrow \text{Ag}(5sp)$ interband transitions in the "plasmonic" region, with their relative intensities controlled by the Ag/Au mixing ratio.

COLL 790

How Hot is the Plasmonic "Hot Spot"?

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Surface plasmon resonance (SPR) excitation on metallic nanostructures can greatly increase the rate of non-radiative decay of excited conduction electrons, resulting in an increase of the local temperature of nanostructure asperities. To date, directly measuring the SPR-induced local temperature change on single plasmonic nanoparticles still remains as a challenge due to the lack of a suitable technique. Herein, we demonstrated a novel graphene-based thermometry technique to explore the SPR-induced temperature change on single nanoparticles. We discovered that the LSPR-induced local temperature change of a 50 nm Au nanoparticle can reach as high as 600 K. Moreover, the temperatures of Au nanoparticle can be controlled by varying the incident laser powers. Knowledge of the SPR-induced temperature change on the surfaces of nanostructures will facilitate the use of nanostructures in various desired chemical applications.

COLL 791

Macro-scale colloidal noble metal nanocrystal arrays for refractive index-based sensing applications

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Noble metal nanocrystals are very promising for sensing applications, because their plasmon resonances are highly dependent on the surrounding environment. However, their practical applications are hindered by the poor stability of the colloidal solutions and the high cost of single-particle spectroscopy. We have developed a new method for directly depositing colloidal metal nanocrystals from solutions onto different substrates. The resultant nanocrystal arrays are uniform and dense, with the single-layer absorbance value reaching 0.4 and the size up to one decimeter square. We characterized the refractive index sensitivities of Au nanorod arrays with and without capping molecules (CTAB, PEG) deposited on glass slides, mesoporous silica and titania films. The nanorods on the titania film exhibit the highest index sensitivity. Furthermore, the nanocrystal arrays can be transferred to various substrates (silicon, graphene, plastics). Our method is expected to greatly facilitate the plasmonic applications that require the formation of large-area metal nanocrystal arrays.

COLL 792

A chiral DNA-assembled gold nanostructure for biosensing

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Plasmon rulers consisting of two optically coupled metal nanoparticles linked by biological macromolecules have provided a tool for bio-imaging and enzymology that is non-bleaching, non-blinking, and biocompatible. To expand this technology to visualize

the subtle conformational changes ubiquitous in biological systems, three-dimensional multicomponent nanoparticle assemblies are required. We report a chiral DNA-mediated nanoparticle assembly which exhibits circular dichroism (CD) and provides a unique substrate for detecting handedness in biological events. We calculated the optical response of metal nanoparticle assemblies using a coupled dipole model. Based on this model, we designed and synthesized a distorted DNA tetrahedron decorated with two 10 nm and two 20 nm diameter gold nanoparticles. A shorter side breaks the mirror plane, forming a chiral assembly. Calculations show that changes in the length of the shorter, symmetry breaking arm of the tetrahedron will change the intensity and spectral position of the CD, even inverting the handedness completely.

COLL 793

Solution Based SERS Detection of Ultra-Low Levels of Dithiocarbamate Fungicides Using Dogbone Shaped Gold Nanoparticles

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It is necessary to detect many types of pesticides at ultralow levels (<1 ng/mL) for maintaining EPA environmental safety standards. Thiram and ferbam are dithiocarbamate fungicides widely used in the field and in harvested crops. Surface enhanced Raman spectroscopy (SERS) is a phenomenon that results in greatly enhanced Raman signals when Raman scattering molecules are bound to metal substrates or to metal nanoparticles. We have developed a solution based direct readout SERS method using dogbone shaped gold nanoparticles for detection of dithiocarbamate fungicides in deionized water, tap water, apple juice, grape juice, and V8 juice. The SERS intensity of the CN stretching mode is monitored as a function of different concentrations of thiram and ferbam bound to the gold nanoparticles. We have obtained dose-response plots and calculated the limits of detection (LODs) for thiram and ferbam using our novel SERS based colloidal direct readout method.

COLL 794

A versatile strategy for gold nanoparticle-enhanced Raman spectroscopy

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Since the mid-1970s surface-enhanced Raman scattering (SERS) has gone through a tortuous pathway to develop into a powerful diagnostic technique because the versatility of SERS has been questioned frequently. Only Au, Ag and Cu and alkali metals can provide the huge enhancement, which has limited the breadth of its practical applications. Based on the fact that SERS is nanostructure- and SPR-enhancement

phenomenon, we have rationally designed various nanostructures to break the limitation of materials generality. Recently we have developed a new operation mode named as Shelled-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS). We chemically synthesized Au or Ag nanoparticles coated with ultra-thin shells (ca. two to four nanometers) of chemically inert silica. Such nanoparticles are spread over the probed substrate of virtually any materials and any surface morphology. High-quality surface Raman spectra were obtained on various molecules such as hydrogen, chloride, sulfate, water and carbon monoxide adsorbed at single-crystal surfaces of different metals. The other studies on membrane components of living cells, pesticide residues on fruits or vegetables and interfacial structure of dye-sensitized solar cells illustrate that SHINERS significantly expands the flexibility of SERS for wide applications in surface, materials, energy and life sciences.

COLL 795

Materials for the selective increase of the Raman intensity of the P=O stretching mode of nerve-agents: A Density Functional Theory based approach

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Nerve-agents (NAs) are extremely toxic chemical warfare. They have been found to contaminate environments because of their solubility in water, and adsorption on silicates, clay materials, paints and cement surfaces. Thus, effective detection of NAs is an important research area. The selective enhancement of the Raman intensities of the P=O stretching mode ($RI_{P=O}$) of NAs through binding with metal/oxide-supported metal surfaces could be considered as a way of detection of such materials. A detailed theoretical investigation has been carried out at the density functional level of theories to investigate the nature of the $RI_{P=O}$ of DFP (diisopropylfluorophosphate, a model NA), bound to MgO, CaO, different gold (Au_8 , Au_{20}) and oxide-supported gold ($MgO...Au_4$, $CaO...Au_4$, $TiO_2...Au_4$, $Al_2O_3...Au_4$, $M_{16}O_{16}...Au_8$, and $[M_{16}O_{15}...Au_8]^{2+}$, $M = Ca, Mg$) clusters. When DFP attaches to the exposed gold atom of such materials through the P=O bond, its polarization occurs (due to charge transfer) to a varied degree depending on the environment of the gold cluster (pure or oxide-supported). The computed $RI_{P=O}$ s in such cases actually show a linear correlation with the P=O bond polarization. This chemical effect is a key factor to choose materials for resonance Raman spectra (RRS). The RRS calculations on the $Au_n...DFP$ ($n = 8, 20$), $M_{16}O_{16}...Au_8$ and $[M_{16}O_{15}...Au_8]^{2+}$, $M = Ca, Mg$) clusters reveal that the $RI_{P=O}$ enhancement could be made quite large and selective. This feature is unique to the NAs, and could be used as a property for their detection.

COLL 796

Nitrate reduction pathways on Cu single crystal surfaces: Effect of oxide and Cl⁻

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The origin of differential nitrate reduction activity between the (100), (111), and (110) faces of Cu is examined using vibrational spectroscopy and calculations. Shell isolated nanoparticle enhanced Raman spectroscopy (SHINERS) reveals that the priming action of nitrate to nitrite reduction concomitant with partial oxidation of the Cu surface, particularly on Cu(111) and Cu(110), is critical to the reduction pathway by facilitating subsequent NO_x reduction. Calculations show that the trend in activity between the different single crystal faces of Cu follows the strength of the adsorption of intermediates on the corresponding oxides; this trend was not found in calculations on the bare metal surfaces. Decoration of the surfaces with Cl⁻ suppresses surface oxidation, resulting in higher overpotentials and lower current density. NH₃ is observed by SHINERS as a direct nitrate reduction product in the presence of Cl⁻, rather than NO_x species, indicating a reaction pathway unique from the undecorated surface.

COLL 797

A Chemically Driven Molecular Switch

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1,4-phenylene diisocyanide (PDI) self-assembles on a Au(111) surface to form one-dimensional oligomeric chains that comprise repeating -(Au-PDI)- units by extracting gold atoms from low-coordination sites on the gold substrate. Exposing a PDI-saturated Au(111) surface to carbon monoxide causes one end of the PDI linker in the surface oligomer to be displaced, thereby interrupting the oligomer chain. Since PDI maintains its pi conjugation throughout the molecule, the oligomer is expected to be electrically conducting. This is confirmed by using the self-assembly chemistry of PDI to bridge between gold nanoparticles on an insulating substrate. This results in an increase in conductivity of the nanoparticle array by more than an order of magnitude consistent with the particles having been bridges by the -(Au-PDI)- oligomers. Exposing this sample to CO causes a change in resistance consistent with the displacement effect of CO found on PDI-saturated Au(111).

COLL 798

Equilibrium gold nanoclusters quenched with biodegradable polymers

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Significant interest exists in understanding the assembly of primary metal nanoparticles into biodegradable nanoclusters exhibiting intense near-infrared (NIR) extinction. Herein, we present the novel concept of equilibrium gold nanoclusters, in which nanocluster size is tuned by appropriately controlling colloidal interactions with a biodegradable polymer. Nanoclusters are synthesized by mixing a dispersion of primary, ~5 nm Au nanospheres with controlled surface charge with a polymer solution and then evaporating the solvent. Nanocluster size is tuned from 20 nm to 40 nm by varying gold and polymer concentrations. Adsorption of the polymer on the nanocluster surface quenches the nanoclusters at an equilibrium size. Biodegradation of this quencher results in nanocluster dissociation to primary nanospheres. Nanocluster size is predicted semi-quantitatively, using a free energy model which balances short-ranged van der Waals and depletion attractions with longer-ranged electrostatic repulsions. The small interparticle distances within the nanoclusters produce strong NIR extinction ideal for biomedical imaging.

COLL 799

Tuning mechanics and surface chemistry independently in biomaterial scaffolds to modulate cell behavior

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The role of extracellular matrix factors (e.g., mechanics, chemistry) in regulating cell behavior is widely accepted. However, decoupling their independent contributions has been challenging. Thus, biomaterials that provide near independent control of mechanics and chemistry to examine cell behaviors are desirable. To this end, we developed a core-shell electrospun nanofiber platform that permits systematic study of the effects of mechanics and surface chemistry on a model cell system: glioblastoma multiforme (GBM) brain cancer cells.

Nanofiber mechanics was independently modulated using different polymers (gelatin, polyethersulfone, polydimethylsiloxane) in the 'core' of the fiber with a common poly(ϵ -caprolactone) (PCL) 'shell'. These materials revealed GBM sensitivity to nanofiber mechanics. Similarly, modulating nanofiber surface chemistry using hyaluronic acid (HA) in the 'shell' with a PCL 'core' revealed GBM sensitivity to HA, in which a negative

effect on migration was observed. These nanofibers are currently being integrated with hydrogels to study cell behaviors across biomaterial interfaces.

COLL 800

Nanopatterned and bioactive stimuli-responsive polymer surfaces: Design and biomaterials analysis challenges

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This presentation will provide (i) recent development of stimuli responsive surfaces that exhibit dynamic structure on lateral length scales of the order of 10 microns and below, (ii) results from study of bioadhesion and biorecognition on these surfaces, (iii) discussion of challenges in analysis of the chemical nature of these surfaces. Stimuli responsive polymer surfaces include patterned polymer brushes and elastomers; biological systems of interest include protein solutions, adherent mammalian cell lines, as well as marine and infectious bacteria. This talk will provide our latest advances in this line of study, as regards to methods for preparing dynamic, structured stimuli responsive surfaces, characterization of their structure and dynamic behavior, along with molecular and cellular biointerfacial phenomena.

COLL 801

Directing the Immune Response Through Biomaterials Engineering

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The immune system has remarkable potential for providing specific and persistent treatment of a range of diseases. Many current immunotherapy approaches include the activation and expansion of T lymphocytes, key mediators of the adaptive immune response. This is accomplished using solid supports to which activating antibodies to the T cell surface receptors CD3 and CD28 are attached. As a major new frontier for biomaterial design, we demonstrate that T cells can respond to the mechanical rigidity of this support, modulating a range of cellular functions including cytokine secretion and proliferative potential. T cells show additional modulation of these functions in response to surface patterning over a range of spatial scales. Importantly, these responses are species dependent. These results will lead to new biomaterials that can tailor the expansion of T cells, capturing additional properties of the native cell-cell communication that leads to T cell activation.

COLL 802

Materials that maintain biological function at injury sites

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When polymeric devices are implanted into vessels, the surrounding endothelial cells are destroyed. Associated complications arise from a combination of cell damage and the foreign body reaction (FBR) at the material surface. Materials that maintain the function of injured cells could simultaneously control the FBR and promote healing. The ability to mimic natural functions that are compromised during surgical procedures is paramount to the development of functional materials for integrated device coatings. In this presentation, the development of natural and synthetic nitric oxide (NO)-releasing materials will be discussed. Nitric oxide naturally promotes the regeneration of cells and controls platelet interactions. Therefore, the development of material coatings that maintain this function at the site of device implant will prevent unwanted biofouling while maintaining homeostasis. Results from both surface analysis techniques and elution studies suggest that the improved performance of the material is a result of the NO release from the surface.

COLL 803

Short peptide-conjugated copolymer based biosensor for specific binding of immunoglobulin G

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We report on a system based on gold sensors decorated with peptides supported in organic layers for the selective detection of human immunoglobulin G (IgG). A random copolymer composed of primary amines containing segment and antifouling segment, poly (2-aminoethyl methacrylate hydrochloride-co-2-hydroxyethyl methacrylate) (poly(AMA-co-HEMA)) was grafted from initiator-coated gold substrates by surface initiated polymerization, followed by immobilization of acetylated-HWRGWVA peptide with specific binding affinity to IgG via amide chemistry. The developed biosensing platforms were characterized by a series of analyses and the extent of binding and binding selectivity for target IgG molecules as well as the capability to minimize non-specific interactions with other proteins were examined by quartz crystal microgravimetry (QCM) and surface plasmon resonance (SPR). It is found this sensor exhibits specific binding capability of IgG with a detection limit as low as 0.05 mg/mL while maintaining excellent non-specific protein resistance.

COLL 804

Improved antifouling property of polyacrylamide with pendent hydration groups

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Molecular structure of nonfouling polymers regulates surface hydration, which well correlates with their antifouling ability. Here we develop and apply in-house surface plasmon resonance and ELISA to quantify and compare adsorbed proteins on between polyacryamide-based coatings (e.g. polyHEAA and polySBAA) and polyacrylate-based coatings (e.g. polyHEA and polySBMA). All of four polymers containing pendent hydration groups display superlow antifouling properties, but polyHEAA and polySBAA with amide groups are still superior to polyHEA and polySBMA against nonspecific protein adsorption. MD simulations also confirm that polyHEAA and polySBAA exhibit higher surface hydration than polyHEA and polySBMA, due to the enhanced hydrogen-bond formation via amide group and pendent hydration groups. Additionally, incorporation of acid degradable crosslinker into polyHEAA and polySBAA nanogels enables to achieve acid-triggered control-release of model drugs, while still maintaining their ultrastability and minimal cytotoxicity in cellular culture, which holds great potential for tumor-targeted drug carriers.

COLL 805

Metal ions in the context of nano- and microparticles - toxicity and detection

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Metal ions in the context of nano- and microparticles are relevant for cells because of two reasons. First, in particular inorganic nanoparticles can contain metal ions which upon corrosion of the particles can be released and cause cytotoxicity, such as in the case of CdSe and Ag nanoparticles.[1,2] Second, nano- and microparticles can be used for the detection of metal ions inside cells.[3,4,5] Following a general introduction about nanoparticles in the context of in vitro experiments both lines will be discussed.[6]

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COLL 806

Effects of multiplexing small molecule-DNA hybrid linkers on the DNA-directed synthesis of nanoparticle superlattices

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The assembly of gold nanoparticles (AuNPs) into colloidal crystals via programmable DNA interactions has recently been shown to be a versatile method for creating nanoparticle-based superlattices with tunable particle compositions, lattice parameters, and crystal symmetries.¹ A phase diagram has been proposed for the construction of various DNA-linked AuNP lattices by controlling both the hydrodynamic size and number of DNA strands on these particles. We have designed and synthesized a new DNA linker system based on small molecule-DNA hybrids (SMDHs), wherein the incorporation of the small molecule results in a branched DNA strand. When using these branched SMDHs as linkers in the construction of a superlattice, a single hybridized junction between particles therefore comprises multiple DNA duplex connections. This allows us to increase the total number of DNA connections between particles, as well as create differences in the thermodynamics of binding between the SMDHs. In this presentation, we will discuss the thermodynamic properties of this new class of SMDH-AuNP structures and their implications in the formation of different nanoparticle superlattices.

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COLL 807

Therapeutic protein delivery using graphene oxides for tissue regeneration

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We demonstrate that graphene oxides (GOs), which are the two-dimensionally charged nanosheets, can potentially serve as therapeutic protein delivery platforms for tissue regeneration. The GO coating on Ti substrates was realized based on the multilayer fabrication called the *layer-by-layer* assembly, followed by the introduction of therapeutic proteins (bone morphogenetic protein, BMP-2) to the GO-coated Ti substrates (Ti/GO). Particularly, GOs contains the hydrophobic π -conjugated domains in the core GO region and the ionized groups around the GO edges, leading to the significant enhancement of protein adsorption through specific non-covalent interactions. The sustained release of BMP-2 from the Ti/GO substrates was observed over 2 weeks, yet completely maintaining its structural stability and bioactivity. Mesenchymal stem cells derived from human bone marrow were cultured on the Ti/GO with BMP-2 adsorbed and showed improved *in vitro* osteogenic differentiation. Eight weeks after the implantation to mouse calvarial defect models, the Ti/GO/BMP-2 implant device distinctively showed new bone formation when compared with other control groups. GOs are thus demonstrated to be effective platforms for dental implants and/or the controlled protein delivery.

COLL 808

Biomimetic reusable adhesive inspired by the gecko

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We fabricate dry adhesives mimicking the gecko fibrillar adhesive system using conventional as well as unconventional techniques. Synthetic dry adhesives with varying tilt angles in the fibrillar structures are fabricated and the resulting adhesion and friction forces are measured and analyzed using a tribometer. Obvious anisotropic property upon shearing direction is exhibited due to the unique design of arrays with triangle pillars each of which is terminated by thin rectangle tips on the edge. Long term test shows that the adhesive allows for long lifetime and repeated use without significant performance degradation. Adhesion measured from samples with different tilt angles

shows a good agreement with the previous reported peel zone model. Adhesion and friction are measured on surfaces with different roughness. Potential applications of such a synthetic dry adhesive include reusable adhesive tapes and sticky pads on robotic appendages.

COLL 809

Determination of adsorbed protein configuration on material surfaces by in situ chemical modification and mass spectrometric mapping

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In situ chemical modification and mass spectrometric mapping (IC-MSM) is a promising tool for characterizing the orientation and localized structural shifts (collectively termed configuration) in adsorbed proteins. However, the current application of this technique is limited to quantifying the labeling profile of a single population of target amino acid as reactivity rate of labeling is specific to a given amino acid and the type of chemical label used. As a result, a direct comparison of the labeling profile of amino acids modified with different chemical labels may not be feasible and could limit a comprehensive understanding on the configuration of adsorbed protein using IC-MSM. In our study we have developed a quantification technique which would allow a direct comparison of the reactivity rate of multiple amino acids which could subsequently aid significantly improving the capabilities of IC-MSM as a tool for characterizing the configurational shifts in adsorbed protein on different surfaces.

COLL 810

Modification of porous templates for patterned 1D metal nanoarchitectures: Directed assemblies of colloid particles, nanolithography and glucose biosensors

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The confined channels of porous Si wafer and anodic alumina membrane can be modified with a method based on directed assemblies and nanolithography. The 1D porous wire arrays, colloid crystal wires, as well as patterns of nanowires and nanotubes can be constructed conveniently. The metal nanowire and nanotube arrays can be utilized as novel electrodes to design biosensors for detecting glucose free of enzyme.

COLL 811

Swelling behaviour of xanthan-based hydrogels

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In this work xanthan chains were crosslinked by esterification reaction at 165 °C either in the absence or in the presence of citric acid. Higher crosslinking density was obtained using citric acid, as evidenced by its lower swelling degree. Tensiometry, a very precise and sensitive technique, was applied to study swelling rates and diffusion mechanisms of water, which was initially stereoselective, controlled by wicking properties, changing to Fickian or Anomalous, depending on hydrogel composition. Hydrogels swelling degree increased at high pH values, due to electrostatic repulsion and ester linkages rupture. Equilibrium swelling degree was affected by salts, depending on gel composition and kind of salt. Effects could be explained by interaction between ions and polymeric chains, EPA/EPD ability of water or osmotic gradient.

COLL 812

Colloidal Synthesis and Magnetism of Chromium-based Chalcospinel Nanocrystals

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Cr-based chalcogenide spinels CuCr_2S_4 , CuCr_2Se_4 and CuCr_2Te_4 are metallic with T_C 's of 377, 430 and 360 K, respectively. Because of their high Curie temperatures, these materials are potential candidates for spin-based electronics and other applications. Nanocrystals of the room temperature magnetic spinel CuCr_2S_4 have been synthesized using a facile solution-based method for the first time. The synthesis involves hot injection of an excess of 1-dodecanethiol (1-DDT) into a boiling coordinating solvent containing CuCl_2 and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The synthesized material is superparamagnetic at room temperature, but exhibits ferromagnetic behavior at low temperatures. We have extended the work to the synthesis of $\text{Cu}_{1-x}\text{Co}_x\text{Cr}_2\text{S}_4$ ($x = 0-1$) nanocrystals over the entire composition range. While CuCr_2S_4 is a ferromagnetic metal, CuCo_2S_4 is known to be ferrimagnetic semiconductor. Systematic changes in the lattice parameter, morphology and magnetic properties of the nanocrystals are observed with composition. The nanocrystals are magnetic over the entire range, with a decrease in the magnetic transition temperature with increasing Co content.

COLL 813

Effect of clay structure on rheology of Epoxy nano-composites

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Polymer based nano-composites reinforced with a small amount of nano size clay particles (<5 vol.%) significantly improve the mechanical, thermal and barrier properties of the pure polymer matrix. They can be differentiated into one with a phase separated composite with properties similar to traditional micro-composites or one with an intercalated nano-composite formed by diffusion of extended polymer molecules between unchanged clay sheets or having exfoliated structure when all the layers are homogeneously dispersed maximizing thus the polymer–clay interactions. Both the swelling of the clay by the epoxy polymer before cure and the intercalation during cure are affected by the chain length of the interlayer exchanged ion. Factors found to improve exfoliation include: lower charge density on the clays, a sufficiently long alkyl ammonium chain length, the use of primary or secondary onium ions and higher cure temperatures. The exfoliated structure mainly leads to an improved modulus, while the remaining stacked structure of intercalated clay platelets is the key to improve toughness.

Dispersion is significantly improved by functionalizing the inorganic filler and thus increasing compatibility between the two phases. Many factors can influence the dispersion and exfoliation of the nanoparticles in the polymer. The final properties of the nanostructure will mainly depend on the choice of the mixing technique and the resulted degree of exfoliation of the nano-clay platelets. Techniques such as in situ polymerization, solution mixing, or sonication (high shear mixing) are widely used to disperse nanoparticles in epoxy. Nano-composites of epoxy and of cross-linked epoxy were prepared with Cloisite 10a (sodium salt of montmorillonite functionalized either with dimethyl, benzyl, hydrogenated tallow, quaternary ammonium) or Cloisite 20a (dimethyl, dehydrogenated tallow, quaternary ammonium). Linear and nonlinear rheological properties are consistent with a network of exfoliated structures possibly facilitated by hydrogen bonding.

COLL 814

Surface gradients via electrochemically activated "click" chemistry: Reactivity mapping and shape control at the micron scale

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Studying and controlling reactions at surfaces is of great fundamental and applied interest in, amongst others, biology, electronics and catalysis. Monolayers are an excellent platform to investigate interfacial reactions and reactivity because of the ability to precisely control surface composition.

Here we focus on the electrochemical production of solution gradients of a catalyst (Cu(I)) for controlling and monitoring the reactivity of the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) at surfaces in space and time in a high-throughput

manner. Using this method, the reaction order in Cu(I) could be determined and spatially visualized in a 2D reactivity map.

Furthermore, we demonstrate that changing the reaction conditions of the CuAAC reaction (e.g. catalyst and/or ligand concentration, reaction time, applied potential difference, etc.), we exert control over the shape of the micron-scale surface gradients, in terms of steepness and surface density. By means of this technique, we attest the fabrication of bi-component and bio-molecular gradients.