Solvation of cations in biological channels

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Sodium and potassium ions are among the most abundant alkali metal ions in aqueous solution and the details of the interactions of these ions with water are crucial for understanding diverse chemical and biological processes. Of note is the selective permeability of cation channels, which is thought to rely on subtle structural differences between the hydration shells of Na+ and K+ ions. During the past decade, atomic-level molecular dynamics (MD) simulations have been used extensively to study K+-selective ion channels. As a result, a picture of the molecular mechanism became available suggesting that the selectivity filters (SF) of ion channels are finely tailored to mimic the structure of the first solvation shell of the permeant cation. The recent structure determinations of Na+-selective channels provide further support to the notion that the first solvation shell of cations plays a key role in selectivity. However, atomistic MD studies show that, in contrast to K+ channels, Na+ binds to the SF of Na+ channels in an almost fully solvated form, seemingly disproving the hypothesis that hydration-shell mimicry plays a major role. Multi-dimensional free energy calculations unveil a more complex role of solvation in ion conduction: while in K+ channels permeation occurs through a concerted displacement of waters and ions across four distinct sites, in Na+ channels diffusion of ions through the SF is less constrained and is related to a dynamic remodeling of the solvation shell of a pair of weakly coupled Na+ ions.

Ultrafast probes of excess charge solvation in anionic water clusters

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The mode of solvation of the excess electron in water clusters has remained controversial from the earliest measurements of the species until the present day. The primary concern lies in whether the excess electron is localized in the cluster interior, in a form which could be considered a nascent hydrated electron, or whether it is localized on the surface of these clusters, in a structure quite distinct from that in the bulk solvent. This talk will report on a series of mixed quantum-classical simulations that address both the structure and electronic excited state lifetimes of anionic water clusters. The results will be compared directly with experiment, and the results will be contrasted with
those obtained for electrons solvated by methanol clusters for which one might anticipate similarities.

**COLL 3**

*Electronic excitation-induced solvation dynamics in liquid water: Molecular analysis of the energy flow pathway and timescales*

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We have recently developed a general work and power analysis scheme to unravel the (generally ultrafast) energy fluxes taking place after excitation of solute modes. This approach has allowed the clarification of the energy pathways for vibrational and rotational relaxation in neat liquid water, showing which solvent modes/hydration shells absorb the excess energy and in which sequence, thus providing a picture of the energy transfer pathway. As we noted in those efforts, the same approach should work in, and bring a new molecular level perspective to, the much-studied ---both experimentally and theoretically--- case of ‘solvation dynamics’ following electronic excitation of a solute.

We have examined the familiar case of a neutral monatomic solute, immersed in water solvent, which is subjected to a sudden acquisition of a unit charge, but considered in a nonequilibrium perspective as opposed to a more common equilibrium time correlation function approach. The path and time scales of the subsequent energy flow to the different degrees of freedom (translational, rotational, vibrational) of the water solvent are analyzed in detail via the work and power analysis scheme, as are the contributions from different hydration shells, and rotational axes. The relation to linear response theory is also analyzed.

**COLL 4**

*Enhanced simulations with solvation: Implicit and explicit*

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The variational implicit solvation model (VISM) has been developed recently and allows for an integrated treatment of apolar and polar interactions. VISM has been advanced to the point that simulations of proteins and their ligands are now possible, so that the method shows promise in drug discovery applications. In the area of explicit solvent simulations, Accelerated Molecular Dynamics (aMD) methods have been developed to enhance sampling by modifying the potential energy surface in ways that allow rigorous recovery of equilibrium properties corresponding to the original potential. aMD is
remarkably effective in probing long-timescale fluctuations in explicitly solvated proteins and has already proven valuable in applications to drug discovery. More information can be found at http://mccammon.ucsd.edu/

COLL 5

Solvation and structure for systems with strong Coulomb interactions

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We propose a new theoretical description of solvation in polar fluids like water and in charged ionic fluids as well based on Local Molecular Field (LMF) theory. LMF theory introduces a general mapping that accurately relates the structure of a nonuniform system with long-ranged intermolecular interactions in an arbitrary external field to that of a simpler "mimic system" with short ranged interactions but in an effective or renormalized field that accounts for the averaged effects of the long ranged interactions. To describe solvation, we can let the external field represent the interaction of the solvent with a fixed arbitrarily complicated and possibly charged solute, and determine the change in free energy as the field is turned on. The analogous solvation free energy can be determined more easily in the short ranged mimic system with no overhead from conventional Ewald sum and related methods usually used to treat Coulomb interactions. Using a thermodynamic cycle we then derive a very simple and analytic expression for the difference in solvation free energy between the full long ranged system and the mimic system. The theory gives very accurate results for the solvation of both hydrophobic and hydrophilic solutes of varying sizes in water and provides qualitative insight as well. The relation between LMF solvation theory and other well founded statistical mechanical approaches like classical density functional theory and quasichemical theory will be discussed.

COLL 6

Structure, fluctuation, and function of biomolecules in solution explored by the 3D-RISM/RISM theory

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There are two physicochemical processes which are essential for living bodies to maintain their life: “self-organization” and “molecular recognition.” Protein folding and formation of cell-membrane are typical examples of the former process, in which biomolecules have to overcome the entropy barrier to organize themselves into some characteristic structure. On the other hand, a molecular recognition process concerns whenever a biomolecule performs its function as a “molecular-machine.” For examples, in order for the enzymatic reaction to occur, substrate molecules should be accommodated first by the protein in its reaction pocket to form so-called an enzyme-
substrate (ES) complex. The two processes may not proceed spontaneously if biomolecules and ligand molecules are existing by themselves in “vacuum,” because those are not in favor with respect to entropy. For instance, the protein folding is a process in which a protein folds into a native conformation, the state of least entropy, from the random coil, the state of largest entropy. Then, why do those processes occur spontaneously in our body? It is because there is always “aqueous solution” in the real environment of a living body.

We have been developing a statistical mechanics theory called "3D-RISM/RISM" for past few decades, which has proven itself to be capable of handling such processes stated above in biosystems. [1] The latest development of the theory has brought the structural fluctuation of biomolecules within scope of the science, which plays a crucial role in any biological activities. [2]

In the talk, I will provide a brief review of our study on biomolecular processes in solution based on the 3D-RISM/RISM theory, and address the new horizon in the statistical mechanics of solution.

References


COLL 7

Charge separation and recombination at nanoscopic interfaces within colloidal quantum dots

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This talk will discuss the relationship between the organic/inorganic interfaces within colloidal semiconductor nanocrystals (quantum dots) and the probability and rate of charge transfer across those interfaces. This rate is dictated by factors such as the degree of delocalization of the charge carrier within the quantum dot, the mobility of the charge carrier within the ligand shell, the surface chemistry of the quantum dot, and the spin multiplicity of the radical ion pair formed by electron transfer. Multi-electron transfer relevant to catalysis will also be discussed.

COLL 8

Fluorescence lifetime spectroscopy and imaging study of the interactions between luminescent quantum dots and binding peptides
Toxicity of nanoparticles has become a significant environmental and health concern as nanotechnology applications continue to grow and they become integral components of consumer products. While binding of nanoparticles to proteins is often a first step in their mechanism of toxicity, a very limited number of studies have addressed nanoparticle-protein interactions in a quantitative manner. The objective of our study is to gain quantitative understanding of these interactions. The study focuses on the interactions between proteins and luminescent semiconductor quantum dots, a class of luminescent nano crystals that has found numerous applications ranging from biomedical imaging to photovoltaic cells and devices. Taking advantage of the unique luminescent properties of semiconductor quantum dots we are using fluorescence lifetime spectroscopy and imaging studies to measure in real time the binding kinetics of model peptides to CdSe/ZnS quantum dots. The presentation will describe the capability of fluorescence lifetime spectroscopy and imaging method to carry out real time kinetic measurements and to obtain the binding constant of peptides to nanoparticles with high sensitivity. The effect of peptide composition, length, and charge on the binding kinetics of peptides to CdSe/ZnS nanoparticles will also be described.

**COLL 9**

**Engineered nanoparticle interaction with living and model bacterial cell membranes**

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Minimizing the unintended consequences of nanomaterial entry into natural environments is of growing interest as the production and commercial use of these novel materials grow. Environmental risk is often evaluated on a case-by-case basis using model biological systems and simple toxicological endpoints. While valid and useful, this approach has limited capability to predict risk. In contrast, our approach is to study more generally the nanomaterial-biological interface, with a focus on the cell membrane. Here we use the single celled bacterium *Shewanella oneidensis* as a model biological system, chosen to minimize biological complexity while maximizing environmental relevance. Specific hypotheses generated through observation of the bacterium-nanoparticle interface are further evaluated in mirrored experiments on supported lipid bilayers. This dual approach results in complimentary data sets that describe the response of a living or model organism to nanomaterial exposure under identical conditions, providing both realistic and fundamental insight into the
nanomaterial-biological interface. This approach is used to identify basic rules that can predict risk and inform the design of more environmentally-friendly nanomaterials.

**COLL 10**

**Transformations of ligand-protected inorganic nanoparticles at interfaces**

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Engineered nanoparticles are often deliberately placed at interfaces (e.g. on fabrics, devices or surfaces) or deposited to form interfaces through adsorption or agglomeration. Once at an interface, a nanoparticle may continue to transform and that transformation may be altered by its presence at the interface. To understand the interfacial transformations of nanoparticles, we have prepared a series of metal and metal oxide nanoparticles with well-defined organic shell coatings. The structures of these materials, and the way in which they are attached or assembled at an interface, are designed to enable us to elucidate how their structural features and environmental conditions influence the transformations of the nanoparticles. We have developed analytical approaches to examine the reactivity of the ligand shells and inorganic cores at interfaces using a combination of transmission electron microscopy, x-ray photoelectron spectroscopy and thermal analysis methods. Here we report the transformations of metal and metal oxide nanoparticle cores and the influence of the ligand shell on those processes.

**COLL 11**

**Interaction of metallic and semiconducting nanoparticles with model cell membranes**

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Lipid membranes form the boundary between living cells and their environment. Nanoparticle uptake into cells requires attachment to and penetration of lipid membranes. Furthermore, nanoparticle interaction with lipid membranes may initiate signaling cascades or membrane disruption that lead to adverse biological outcomes. Prediction of the effect nanoparticles on organisms requires a molecular scale understanding of their interaction with biological membranes. Using model cell membranes of varying complexity we have investigated the effects of lipid membrane composition, nanoparticle surface functionalization, solution chemistry, and acquired “coronas” of intact and biogeochemically processed biomolecules on metallic and semiconducting nanoparticle interaction with lipid membranes. Nanoparticle interactions with model membranes were studied by quartz crystal microbalance with dissipation monitoring, optical waveguide lightmode spectroscopy, non-linear optical spectroscopies, and fluorescence microscopies. We demonstrate the interaction of nanoparticles with specific membrane components and identify lipid-nanoparticle-solution combinations that lead to attachment despite electrostatic repulsion and to membrane disruption.

COLL 12

Thermal stability of CdSe/CdS quantum dots and their application as a novel geothermal tracer

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Quantum dot nanoparticles (QDs) have been widely researched in material science for the past two decades due to their unique size-dependent properties. By modifying the surface chemistry of QDs their interaction with other materials can be controlled, making them attractive as potential biological markers, solid-state lighting systems, or for use in solar cells. Expanding work in QD research has necessitated a better understanding of how they transport through subsurface water regimes in order to predict contamination extent but has not been used to characterize subsurface reservoirs. The shift of the characteristic emission peak due to small changes in the QD diameter creates a potential range of tracers with unique optical signatures but similar transport and thermal stability properties. The large residence times of existing tracers in highly fractured reservoirs means this could be valuable to subsurface reservoir characterization. By modifying their surface chemistry, it is possible to create temperature stable QDs that can be used as tracer particles to characterize high-temperature porous media systems. These QDs are synthesized using a one-pot aqueous method and then undergo surface additions of sodium citrate ligand before being heated in an autoclave reactor to geothermal reservoir temperatures. Temperature stable QDs were then pumped through high-temperature columns of Ottawa sand to study their transport and retention properties.
Bioactive and stimuli-responsive nanopillars to spatially and temporally stimulate cells at the sub-cellular level

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Recent developments in stem-cell related regenerative medicine have raised requirements for an accurate control of cell–material interaction at the nanometer scale. Surface nanostructures were notably shown to be of a great interest to trigger cell functions. Among the relevant 3D nanostructures, nanopillars showed the unique capability to penetrate into cell interior which can be advantageously used to perform local drug delivery.

Here we report on the development of nanopillars¹,² functionalized with redox-responsive copolymer layers leading to a local and temporally controlled administration of drug into cells (figure 1). Thiolactone-based copolymers³,⁴,⁵ releasing free thiol groups in presence of amine derivatives were successfully grafted onto gold nanopillars and flat gold surfaces used as controls. The resulting redox-responsive layers were subsequently modified with a fluorescent thiol derivative through a cleavable disulfide link. The microstructure, chemical composition, stability and redox-responsive properties of copolymer layers were systematically investigated as a function of their content in thiolactone units. Moreover, the ability of the modified surfaces to release a labeled substance under redox stimulation was demonstrated in physiological conditions. Finally, first tests were performed in presence of cells.
Design principles and properties of environmentally friendly fluorosurfactants

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Fluorinated surfactants with short perfluoroalkyl chains \((R^F)\) as potential substitutes for the environmentally questionable, long \(R^F\) systems are presented. Three types of nonionic hydrophilic-fluorophilic amphiphiles are synthesized and evaluated based on surface activity in equilibrated (static) and non-equilibrated (dynamic) states. Furthermore, several mono- and disaccharide-based fluorosurfactants are also examined as potential non-bioaccumulative alternatives. A correlation between the chemical structure and resulting surface properties is made by comparing \(R^F\) length, number and size, alkyl-spacer, and hydrophilic moieties. Based on dynamic and static surface tension experiments, the effects of surfactant structure are summarized to
provide a basis for the future design of fluorosurfactants. We have found that surfactants with more perfluorinated chains tend to have a higher surface tension reduction, but typically result in slower dynamic behaviors. Using the presented structural characteristics, surfactants with $R^F < 4$ can be prepared with static surface tensions as low as 18.1 mN/m or reduce surface tension within milliseconds.

**COLL 15**

**Fundamental properties of natural surfactants for effective oil/water dispersions**

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Functional surfactants from natural materials have the advantage of being biodegradable and can be obtained through sustainable agriculture. We have studied the properties of functional natural surfactants obtained from the *Opuntia ficus indica* cactus as dispersants of crude oil droplets in water (O/W emulsions), in both fresh and seawater. We studied the effect of oil concentration and surfactant concentration on droplet size and stability, as well as on the critical micelle concentration. Since emulsification is caused by the stirring of an oil/surfactant/water system, the dynamic equilibrium of the droplets inducing their rupture and coalescence depends on the formulation and composition variables, mixing characteristics and preparation conditions. Three extracts of this cactus plant have been studied for their effectiveness as dispersants and have been compared with those from Corexit 9500, which is a commercial dispersant for crude oil. We found that these natural surfactants effectively dissolve heavy and light crude oil from the air-water interface of a water column for rapid biodegradation. We determined that the amount of natural surfactants needed to obtain optimal dispersion stability is lower than that needed of Corexit. We also determined the droplet size and size distribution of the dispersed phase as a function of the dispersant to ratio depends on surfactant composition. These characteristics are important to understand the effective use of natural dispersants and its intrinsic character to modify interfacial properties and to improve their dispersion efficiency. We expect the use of natural dispersants will have a positive environmental, economic, and societal impact in crude oil cleanup operations.

**COLL 16**

**Self-assembly of amphiphilic molecules into various nanostructures under various external conditions: A small angle neutron scattering study**

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Amphiphilic molecules with both hydrophilic and hydrophobic moieties self-assemble into various micellar structures and represent excellent phase behaviors depending on their geometrical molecular shape in aqueous solution. The self-assembly of amphiphilic molecules can easily transform into other structures by controlling the external conditions such as temperature, pH and additives that can induce a different geometrical molecular shape. Therefore, the amphiphilic molecules have attracted considerable interests for a wide range of potential applications such as nanotemplates, nanobuilding blocks or drug delivery. However, for practical use of amphiphilic molecules in nano and bio-science, it is essential to know the information for the phase behavior of amphiphilic molecules under various external conditions. Here, the various self-assembled structures of amphiphilic molecules including surfactants and block copolymers under the additives and temperature change have been investigated by using the small angle neutron scattering (SANS). The SANS intensity showed that the surfactants formed cylindrical micelle induced by the additives even below CMC and transformed into unilamellar vesicles by further increasing the additives. The size of the vesicular structure was increased with their alkyl chain length. Furthermore, the surfactant vesicles transformed into cylindrical micelles by temperature elevation [1, 2]. For the block copolymers, the SANS intensity revealed various nanostructures including spheres, cylinders, and vesicles depending on the hydrophilic mass fraction of the block copolymer and external conditions [3,4]

Reference


COLL 17

Effect of polyelectrolyte concentration, molecular weight, charge localization, and backbone rigidity/hydrophobicity on complex coacervate formation and rheology

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Due to wide range of applications, much emphasis has been placed on understanding the physicochemical behavior of polyelectrolyte/surfactant complex coacervates. In this
study we have explored the correlation of the physicochemical behavior of coacervates normalized with critical overlap concentration of the polymer.

The effect of molecular weight effect was studied for cationic hydroxyethylcellulose. The effect of charge distribution was studied between the randomly charged poly(methacrylamidopropyltrimethyl ammonium chloride)(MAPTAC) and tri-cluster charged poly(methacrylamide propyl (methoxy-carbonyl-methyl)dimethyl ammonium chloride) (AMT). The effect of rigidity and hydrophilicity/hydrophobicity of the polyelectrolyte backbone was studied by comparing and contrasting flexible/hydrophobic MAPTAC and semi rigid/hydrophilic Cationic HEC. All of these polyelectrolytes were interacted with sodium dodecyl sulfate (SDS) surfactant over a wide range of polymer and surfactant concentrations. The adsorption behavior was analyzed by surface tension measurements, while, the complexation in the bulk was examined by rheological measurements. Fluorescence measurement techniques were additionally used to analyze the effect of charge localization on the structure of the polyelectrolyte/surfactant complexes.

Contrary to prior studies, our investigation revealed that above the critical aggregation concentration, the surface tension increased with increase in the SDS concentration and this became more pronounced with increase in polyelectrolyte molecular weight. This increase can be explained by intermolecular association preferentially occurring in the solution phase between the polymer and surfactant through hydrophobic association of the bound surfactants. Increase in molecular weight increased this intermolecular association and the surface tension increased with increase in the molecular weight.

Fluorescence measurements revealed that charge localization enhances SDS aggregation. Rigidity and hydrophilicity of the polymer backbone increased the surface tension in the one phase region. Both the viscosity and storage modulus of the cationic HEC coacervate phase is higher than MAPTAC. We deduce from this that the MAPTAC chain collapses and phase-separates with addition on surfactant in the one phase region.

**COLL 18**

**pH-regulated and pH-reversible Ace(n)-2-Ace(n): Recyclable and environmental-friendly gemini carboxylate surfactant**

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Gemini surfactants, emerging surfactants with unique properties compared with conventional surfactants, have been attracting great attention in both academics and industries. Herein, we studied a new series of gemini surfactants N,N'-dialkyl-N,N'-diacacetate ethylenediamine (hereinafter, Ace(n)-2-Ace(n) for the sake of simplicity). Ace(n)-2-Ace(n)'s surface properties and aggregation behaviors were studied in aqueous solution using pH titration, surface tension, zeta potential, dynamic light scattering (DLS), transmission lection microscopy (TEM) and fluorescence measurements. On the basis of pK\textsubscript{a} values obtained, surface tension was measured, as well as key surface property parameters at three different pH intervals. We summarized the change rule about surface properties among the differing double carbon chains by analyzing physicochemical properties. And the measurement results show that the properties of Ace(n)-2-Ace(n) are not only superior to corresponding monomeric surfactants, but also regulated by pH. The DLS and TEM results preliminarily prove that not only a better-distributed but also a higher quantity of aggregate can be generated in Ace(n)-2-Ace(n) solutions under neutral pH environment. Then steady-state fluorescence spectra of pyrene-surfactant solution was measured to further demonstrate the change of aggregate number in Ace(n)-2-Ace(n) solutions. The pH-controllable Ace(n)-2-Ace(n) was also found to be pH-reversible by cycling light scattering measurement at least three times. Furthermore, emulsion stability of dodecane-in-water in different pH showed that emulsion was inversed between "on" the O/W type under alkaline condition and "off" the W/O under neutral. The double phase inversion is also supported by measuring and comparing the emulsion's conductivities. Thus, this study has shown that, for the first time, a new series of gemini surfactants can be used as pH-regulated and pH-reversible surfactants, which are substantially recyclable and environmental-friendly.
Impact of molecular architecture on lyotropic liquid crystals derived from bis(alkyltriazolium) gemini amphiphiles

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Minimal hydration of small molecule surfactants drives their cooperative and non-covalent self-assembly by virtue of the hydrophobic effect, leading to the formation of lyotropic liquid crystals (LLCs) with periodic nanoscale structures. Characterized by highly tortuous, interpenetrating networks of hydrophobic and hydrophilic channels, bicontinuous LLCs are particularly useful in myriad applications. As a consequence of their non-constant mean curvatures, these bicontinuous LLCs are somewhat difficult to access using traditional single-tail surfactants. Motivated by recent experimental reports that suggest that gemini amphiphiles favor the formation of bicontinuous LLCs, we have studied the synthesis and self-assembly behavior of bis(alkyltriazolium) gemini surfactants bearing I-, Cl-, and NO3- counterions using a combination of optical birefringence and small-angle X-ray scattering. We have found that the hydrophilicity of the counterion controls the size of the composition windows over which LLC phases form. We further show that bis(alkyltriazolium) gemini surfactants furnish access to two non-constant mean curvature LLCs: (1) the inverse gyroid phase, and (2) an unprecedented inverse phase with Pm3(-)n symmetry, comprising tetrahedrally-closest packed micelles. We rationalize our observations in terms of a model, whereby a combination of intra- and inter-molecular electrostatic interactions specified by the surfactant structure and counterion-headgroup hydration guide the formation of these technologically useful phases.

Nanostructured aqueous solutions as green and efficient reaction media

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Surfactant solutions provide a special class of media for conducting chemical reactions. The nanostructuring of reaction media provides an ideal opportunity for tuning the selectivity of chemical reactions where a multiplicity of reaction products is possible. The hydrophilicity/hydrophobicity of the medium varies drastically within a short distance in micelles and microemulsion droplets and the resultant orientation of molecules solubilised by these structures. The orientation coupled with the high
localised concentration of reagent has resulted in changing the selectivity of ortho-
chlorination of phenol by four folds, and substituted phenols by three folds. Deactivated
aromatic molecules such as benzoic acid can also benefit with this technique and 75%
meta-chlorination of benzoic acid could be altered to 85% ortho-chlorination. Heck
reaction, Suzuki reaction and Sonogashira reactions have also benefited from
surfactant solution as media although not through micellar catalysis.

COLL 22

Cationic surfmers and block copolymers for emulsion polymerization

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Combining the properties of surfactants and monomers into a single molecule is highly
advantageous for the synthesis of nanoparticles via emulsion polymerization. The
inclusion of a charged species that is covalently bound to the surface is desirable to
stabilize the particles against coalescence and flocculation. Cationic particles in
particular have a wide range of applications from gene delivery to immunoassays. The
talk will focus on charged monomers within the same family and how their incorporation
affects particle formation and size. Cationic block copolymer stabilizers have also been
explored. Properties such as size, surface charge density, and zeta potential of the
particles will be discussed.
Spatially resolved concentration and segmental flow alignment in a shear-banding solution of polymer-like micelles in steady and oscillatory flow

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The shear rheology and flow behavior of highly entangled worm-like or polymer-like micelles is investigated. We measure the spatially resolved microstructure and concentration in the plane of flow for a viscoelastic solution of polymer-like micelles comprised of mass fraction 6.0% (volume fraction 6.6%) solution of 2:1 molar ratio cetylpyridinium chloride/sodium salicylate in 0.5 mol/L NaCl/D2O through the shear banding transition. Spatially resolved flow small-angle neutron scattering measurements in the velocity−velocity gradient (1−2) plane of flow establish the local microstructure, and scanning narrow-aperture flow ultrasmall-angle neutron scattering (SNAFUSANS) measurements indicate no flow-induced concentration gradients within measurement accuracy. These results show shear banding in this solution is not associated with an isotropic−nematic transition and are fundamentally important for validating models of shear-banding complex fluids. A new experimental method is developed using simultaneous small angle neutron scattering (SANS) and nonlinear oscillatory shear rheometry to investigate the spatiotemporal microstructure evolution. We demonstrate the novelty of nonlinear oscillatory shear experimental methods to create and interrogate metastable material states. These include a precursory state to the shear banded condition as well as a disentangled, low viscosity state with an inhomogeneous supra-molecular microstructure flowing at high shear rates. This new experimental evidence provides insight into the complexities of the shear banding phenomenon often observed in sheared complex fluids and provides valuable data for quantitatively testing non-equilibrium theory.


Dissipative particle dynamics models of self-assembly in surfactant, polymeric, nanoparticle systems

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Nanoscale self-assembly is ubiquitous in colloidal systems, such as micellar solutions and nanoparticle-polymer composites. Transport, mechanical, and rheological properties of a self-assembled system critically depend on the specifics of its morphology, which may possess a hierarchical architecture over a wide range of scales. The central problem in modeling of self-assembled systems is the structure formation on the scales far exceeding the capabilities of atomistic simulations. The paper will present the capabilities of the coarse-grained mesoscopic methods of dissipative particle dynamics (DPD) for modeling complex multicomponent systems. The DPD method has recently received a lot of attention due to its versatility and computational efficiency. However, the application of the DFT method for quantitative analyses requires a set of coarse-grained interaction parameters, which must reflect the specifics of the chemical structure of constituent compounds. We will present a new practical approach to the parameterization of DPD models, which combines coarse-grained Monte Carlo simulation of thermodynamic properties and atomistic molecular dynamics simulation of chain rigidity and conformations. The DPD method will be illustrated drawing on the examples of micellization in surfactant solutions, conformational transformations in polymer brushes, and interactions of nanoparticles with polymer grafted surfaces.

**COLL 25**

**Combining experiment and theory: Atmospheric organics at the air-water interface**

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Surface properties of organic aerosol are poorly constrained, due to the complex nature of their formation and atmospheric aging, as well as due to the practical challenges associated with gaining surface-specific information. However, a better description of the interfacial behaviour of atmospheric organics is critical to understanding the role that organic aerosol plays in influencing climate, human health and air quality. This talk will highlight recent studies of the surface behaviour of atmospherically important oxygen-containing organic molecules in aqueous solutions of relevant composition. Specifically, we demonstrate that molecular structure, pH, and the presence and identity of additional salts, strongly impact the surface adsorption of low-molecular-weight dicarboxylic acids (i.e., malonic, glutaric, and adipic acid) and ketones (i.e., 3-pentanone); structure and aqueous composition play an important, yet somewhat different role in governing the surface adsorption of α-dicarbonyl organic compounds (i.e., methylglyoxal). Significantly, we show that a combined experimental and theoretical approach involving vibrational sum frequency generation spectroscopy (VSFS), surface tensiometry, bulk vibrational spectroscopies, molecular dynamics simulations, and density functional theory calculations, is essential for obtaining a detailed molecular picture of the adsorptive properties of these fundamentally important atmospheric organics.
Phase separation in submicron organic aerosol and consequences for aerosol optical properties

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The morphology of organic aerosol particles has consequences for aerosol optical properties, mass accommodation, cloud condensation and ice nucleation activity, and heterogeneous chemistry. We use cryo-transmission electron microscopy to investigate the phase separation behavior of dry, submicron particles composed of carboxylic acids, organic alcohols, and ammonium sulfate. We have found that phase separation behavior is dependent on the aqueous solubility of the organic compound, where highly soluble organic compounds form homogeneous morphologies and low solubility organic compounds form phase separated morphologies. Organic compounds of intermediate solubility form phase separated morphologies at large diameters and homogeneous structures at small diameters. Using cavity ring-down spectroscopy (CRDS), we have determined that particles with partially engulfed and core shell morphologies have similar extinction cross sections. In addition, we have explored the extent to which CRDS can resolve phase separated and homogeneous morphologies. We will discuss the implications of our results for aerosol radiative properties.

Vibrational sum frequency generation spectroscopy of secondary organic aerosol particle surfaces as a function of relative humidity

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Secondary organic aerosol (SOA) particles have been proposed to undergo phase transitions as a function of relative humidity (RH). While indirect measurements of this process are available in the literature, the surfaces of SOA particles have not yet been probed at high or low RH. Here, we report results from surface-selective vibrational spectroscopic measurements of SOA particles derived from α-pinene in a flow tube and subsequently collected on Teflon filters that were subsequently pressed onto optical windows to transfer SOA particles on to them. SOA particles were also collected directly onto optical windows by electrostatic deposition. The windows obtained from both methods were then placed into an RH-controlled flow cell. Vibrational sum frequency generation (SFG) spectra obtained in the CH stretching region from the surfaces of SOA particles show one dominant spectral feature at 2940 cm⁻¹ that is attributed to a combination of methyl asymmetric and methylene symmetric stretching modes. RH-
cycling experiments reveal that the SFG intensity at 2940 cm\(^{-1}\) is up to 32±6% higher at ∼0% RH than at ∼95% RH. Given that SFG signal intensity reductions are generally associated with increased surface disorder and concomitant loss in net alignment of oscillators, we attribute our observations to substantial increases in surface disorder at high RH. The RH-dependent SFG signal intensity variations decrease in magnitude of observed change in the SFG signal intensity as the particle material density increases.

**COLL 28**

**Computational modeling of aerosol surfaces**

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The structural and dynamical properties of aerosol surfaces play a central role in many heterogeneous processes of relevance in the atmosphere, spanning a wide range of length and time scales. In this talk, I will describe our current efforts aimed at bridging the atomistic scale, where chemical processes take place, with the macroscopic scale over which phase ordering at the aerosol surface occurs. In particular, I will present results from both fully atomistic and coarse-grained molecular dynamics simulations of a series of Langmuir monolayers with increasing complexity representative of the organic layers found on aerosol particles in the troposphere. Particular focus will be on the relationship between structural and thermodynamic properties as a function of surface coverage. The simulation results will be discussed within the context of the available experimental data.

**COLL 29**

**Time-resolved photoelectron spectroscopy on liquid jets**

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Electron solvation in liquids is process of fundamental importance in chemistry, biology, and physics. By performing time-resolved photoelectron spectroscopy on electrons solvated in liquid microjets of water and other solvents, the energetics and dynamics of electron solvation are probed in unprecedented detail. These experiments make use of subtle aspects of the liquid-vapor interface.

**COLL 30**

**Mechanisms of nitrate photochemistry as probed by cavity-enhanced absorption spectroscopy**

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Nitrate and nitric acid on aerosol and boundary layer surfaces are temporary sinks in the cycling of nitrogen oxides in the atmosphere that represent a potentially important reservoir for sustained nitrogen oxide emissions over prolonged periods of time. Despite a number of mechanistic studies over the years, there remain unresolved questions about how species such as nitrous acid can be formed from nitrate on surfaces. In this presentation we show how cavity-enhanced absorption spectroscopy and differential optical absorption spectroscopy techniques are used to obtain insights into the mechanism of nitrous acid fluxes from aqueous nitrate solutions irradiated in the actinic range. The results are expected to improve the ability of models to capture ground-to-air or aerosol-to-air emissions of reactive nitrogen species to the atmosphere.

**COLL 31**

**Methylglyoxal at the air-water interface**

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The formation and evolution of secondary organic aerosol (SOA) is poorly understood, with current models based on the reversible gas-to-particle partitioning of semi-volatile organics failing to reproduce SOA observations. Recently, it has been suggested that aqueous-phase processing of atmospheric α-dicarbonyl compounds such as methylglyoxal (MG) could constitute an important source of SOA. The uptake of MG to aqueous particles is higher than expected due to the fact that its carbonyl moieties can hydrate to form diols, as well as the fact that MG can undergo aldol condensation reactions to form larger oligomers in solution. MG is known to be surface active but an improved description of its surface behaviour is crucial to understanding MG-SOA formation, in addition to understanding its gas-to-particle partitioning and cloud forming potential. Here, we will present results from our investigations of MG adsorption at the air-aqueous interface. This study employs a combined experimental and theoretical approach involving vibrational sum frequency generation spectroscopy (VSFS), surface tensiometry, bulk vibrational spectroscopies, molecular dynamics simulations, and density functional theory calculations in order to obtain molecular-level information about MG’s surface adsorption, orientation and hydration state, in both the presence and absence of salts.

**COLL 32**

**Particle-resolved modeling of the heterogeneous oxidation of soot surfaces**

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The impact of soot particles on public health and climate strongly depends on the per-particle composition, which may be significantly affected by heterogeneous chemical reactions. Here, we consider soot particles coated with polycyclic aromatic hydrocarbons (PAHs) in a polluted urban scenario. We use the particle-resolved aerosol model PartMC-MOSAIC to simulate heterogeneous chemistry on individual particles, focusing on the interaction of the major atmospheric oxidants (O3, NO2, OH, and NO3) with PAHs, including competitive co-adsorption of water vapor. PAH half-lives are on the order of seconds during the night, when the PAHs are rapidly oxidized by the gas-surface reaction with NO3. During the day, PAH half-lives are on the order of minutes and determined mostly by the surface layer reaction of PAHs with adsorbed O3. Despite its high reactivity, OH appears to have a negligible effect on PAH degradation due to its very low concentration in the atmosphere.

**COLL 33**

**Halogen bonding and pyridine coordination as versatile tools for the supramolecular assembly of nanoparticles**

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Supramolecular assembly of gold nanoparticles (AuNPs) in solution and as composite thin films mediated by halogen bonding interactions and pyridine coordination will be discussed. Time-dependent studies showed that the primary formation of small AuNP aggregates by halogen bonding in solution controls the inner structure of large assemblies. The appearance of the overall hybrid structures can be engineered by varying the concentration of organic linkers. We will also demonstrate the fabrication of integrated and segregated Au/γ-Fe2O3 binary nanoparticle assemblies. The structural arrangement of these binary assemblies is a function of the capping layer. The use of orthogonal coordination chemistry resulted in the formation of mixed (integrated) assemblies, whereas the use of nanoparticle-ligand coordination or π–π stacking resulted in well-separated domains (segregated assemblies). This formation of segregated assemblies reflects the importance and the use of hierarchical forces for phase-separation with nanoparticles.
Cell fate is a coordinated response caused by biomechanical and biochemical interactions with the extracellular matrix (ECM). Numerous synthetic gels have been developed as mimics of the extracellular matrix, in the hope of understanding how cells respond to the mechanical properties of the tissue microenvironment, with the goal being to develop a fully synthetic extracellular matrix for regenerative medicine applications. In contrast to all synthetic gels developed to date, the extracellular matrix proteins such as collagen type I, and fibrin, display nonlinear mechanical properties such as strain stiffening and negative normal stress [1]. In these materials the elastic modulus of the gel increases by several orders of magnitude as the applied strain increases such that the resistance that a cell feels is strongly depended of the strain that it applies. In this presentation I will demonstrate the unique cytomimetic properties of hydrogels based on oligo(ethylene glycol) grafted polyisocyanopeptides [2]. These extremely stiff helical polymers [3] form gels upon warming at concentrations as low as 0.005 %-wt polymer, with materials properties almost identical to these of intermediate filaments and extracellular matrices. The macroscopic behaviour of these gels can be
described in terms of the molecular properties of the basic stiff helical polymer and a multi-step hierarchical self-assembly, which results in strain stiffening [4]. The unique ability of these materials and their application in cell growth and drug therapeutics will be discussed.


COLL 35

Functional nanoprobes and assemblies for detection of biomolecules and biomarkers

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The development of nanoprobes to interface not only the targeted molecules but also provide responses to external stimuli is increasingly important for point-of-care detection technologies. We have been investigating functional nanostructures as functional nanoprobes in two related pathways. One involves creation of functional nanoparticles with desired magnetic, electrical, and spectroscopic properties that are dispersed in a solution or assembled on a substrate. Examples of surface-enhanced Raman scattering detection of biomolecules (e.g., DNAs, miRNAs, proteins, etc.) relevant to medical diagnostics will be discussed. The other involves creation of electrically-responsive nanoparticle assemblies on a flexible device as sensing arrays. Examples of flexible chemical sensing of volatile organic compound biomarkers related to detection of human breaths for diagnostics of various diseases will be discussed. Implications of the findings in these two pathways will also be discussed in terms of translating the technologies to point-of-care detection applications.

COLL 36

Mechanical properties of 2D alkanethiol gold nanoparticle membranes

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Membranes formed from self-assembled nanoparticle monolayers have mechanical properties that may make them suitable for use in micro-scale devices. Experimental tests of membranes with different cores and ligands indicate that ligand length as well
as core-ligand and ligand-ligand interactions influence mechanical response of the membrane. Using explicit-atom molecular dynamics simulations, we examine the properties of two-dimensional hexagonal arrays of alkanethiol-coated Au nanoparticles. Results are presented for nanoparticle core diameters from 4-6nm, ligand lengths of 10-18 units, and carboxyl or methyl end groups, all of which influence the mechanical properties of the membranes. Nanoparticle lattice spacing is comparable to those measured experimentally. Simulations indicate that hydrogen bonding can play a significant role in systems with carboxyl-terminated ligands, increasing the equilibrium nanoparticle spacing and significantly increasing the membrane strength in tension, consistent with experimental findings. Membranes formed from carboxyl-terminated ligands can sustain large tensile deformations, while membranes with methyl-terminated ligands fail at smaller strains. Simulations also indicate that interdigitation of ligands from neighboring nanoparticles varies with ligand length and terminal group. Interdigitation is enhanced for longer ligands and for methyl-terminated ligands. This interdigitation can result in an increase in measured elastic moduli. As in experiment, simulations indicate that the response of the deformed membrane is purely elastic with no observed viscous effects. Elastic moduli are measured to be up to 1 GPa for the strongest membranes. These findings represent a systematic approach to evaluating the role of ligand length and composition on membrane mechanical properties. Knowledge of how microstructure and composition influence membrane properties could lead to more efficient membrane manufacture and improved mechanical properties. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

**COLL 37**

**Multicompartiment mesoporous silica nanoparticles with branched shapes from an epitaxial growth mechanism**

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Mesoporous nanomaterials have attracted widespread interest due to their structural versatility for applications including catalysis, separation and nanomedicine. This presentation reports on a one-pot synthesis method for a class of mesoporous silica nanoparticles (MSNs) containing both cubic and hexagonally structured compartments within one particle. These multicompartiment MSNs (mc-MSNs) consist of a core with cage-like cubic mesoporous morphology and up to four branches with hexagonally packed cylindrical mesopores epitaxially growing out of the cubic core vertices. The extent of cylindrical mesostructure growth can be controlled via a single additive in the synthesis. Results suggest a path towards high levels of architectural complexity in locally amorphous, mesostructured nanoparticles circumventing a major roadblock to tuning different pore environments of the same particle for specific chemistries in catalysis or drug delivery.
References:


**COLL 38**

WITHDRAWN

**COLL 39**

From “nanoions” to all-nanoparticle electronics

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Nanoscopic objects stabilized with charged organics exhibit properties fundamentally different from either molecular or macromolecular ions, and can combine ionic-like properties with electronic and ionic conductivity and/or photoexcitability. By careful control of electrostatic interactions, “nanoions” of various shapes and material compositions can be assembled into functional nanomaterials including 3D supracrystals, "layered" crystals, or extended films. Depending on the properties of the charged organics, these nanomaterials can act as chemical amplifiers, photoconductors, diodes, transistors, or even full-fledged electronic circuits containing no semiconductors. This last set of constructs can integrate on the nanoparticles electronic function with chemical sensing.

**COLL 40**

Assembly and integration of heterogeneous micro- and nano-scale building blocks from a microfluidic device

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Novel device concepts in nanoelectronics, optics and bio-sensing based on new materials in the form of micro- and nanoscale building blocks require new fabrication strategies. Structures cannot be carved out of a substrate by conventional top-down fabrication methods alone. New ways of heterogeneous bottom-up integration are required, especially when different micro- and nanoscale components have to be merged. The combination of traditional and novel top-down patterning processes with directed self-assembly is a promising approach that can exploit the best of both worlds.
We use capillary forces of a moving meniscus to direct objects into desired positions on a topographically patterned template. Capillary forces are strong and very sensitive regarding the trap geometry. Thus, high-yield and highly specific positioning of small colloidal objects is possible, even with control of the orientation when shape-anisotropic particles, such as nanorods, are used.

The method of capillary assembly is further advanced by replacing the colloidal drop sandwiched between the template and a cover slide by a dedicated microfluidic device that delivers the colloidal suspension from a slit onto the template. The microfluidic device improves control of the position and the size of the assembly area. In addition, it facilitates a continuous supply of particle suspension for large-area assemblies and enables control of the colloid composition as required for the fabrication of cross-gradients. The simultaneous assembly from two capillary bridges close to each other enables size-selective assemblies and controlled fabrication of particle clusters from different components in a single assembly run. Applications of the microfluidic assembly device and strategies for the transfer and harvesting of particle clusters produced in this way will be discussed.

COLL 41

Spectroscopic microscopy of molecular structure, bonding, and reactivity

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The interrelationship among the structure, bonding, and reactivity of molecules lies at the foundation of our understanding and control of chemistry. The scanning tunneling microscope (STM) can be used for spectroscopic imaging of this interrelationship at the molecular level with atomic resolution. The enabling capability of the STM lies in its ability for topography, manipulation, and single molecule vibrational spectroscopy to image the molecular skeletal structure, intra- and extramolecular bonding, and chemical fingerprinting of the reactants and products.

COLL 42

Deriving functionality from atomically precise structure in metal-organic complexes at 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-based technologies in catalysis, energy conversion, sensors, electronics, and other applications. We have studied the self-assembly of highly-ordered
organic nanostructures at surfaces to develop well-controlled, functional organic and metal-organic layers. Redox-active, on-surface coordination assembly has allowed the formation of well-defined metal centers, which are of interest for hydrocarbon catalysis. Characterization is made by high-resolution scanning tunneling microscopy, X-ray photoelectron spectroscopy, and high-resolution electron energy loss spectroscopy. New measurements of structure-function relationships and reactivity of supported catalyst complexes will be presented. Connections between experimental results and theory are being developed, as are molecular design modifications to tune surface reactivity.

COLL 43

Trends in adsorption energies on well-defined surfaces

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We have recently compiled what we consider to be the most reliable experimental adsorption energies of many species on single crystalline surfaces of metals and metal oxides, as measured by single crystal adsorption calorimetry (SCAC), temperature programmed desorption (TPD) and equilibrium adsorption isotherms (EAI). Trends in those adsorption energies will be discussed, with the aim of providing some predictive ability with respect to adsorption energetics and how they depend on the nature of the adsorbate and the nature of the surface.

Work supported by NSF grant #CHE-1010287 and DOE-OBES Chemical Sciences Division.

COLL 44

Synthesis at the single molecule Level: Polymerization, cyclization, and molecular heterojunctions

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Progress in molecular self-assembly at surfaces has enabled fabrication of increasingly complex molecular nanostructures. This includes graphene-based nanoribbons (GNRs) synthesized via step-growth polymerization from chemically-engineered monomer precursors. Using this technique we have developed a new "N=13" monomer that allows growth of fully cyclized GNRs having a width almost twice the width seen for previous bottom-up-synthesized GNRs, thus enabling the GNR energy gap to be tuned ("N" measures the width of the GNR in terms of carbon atoms). Combining these new N=13 monomers with previously reported N=7 precursors allows bottom-up fabrication
of new GNR-based heterojunctions that exhibit a spatially varying width and energy gap. Such heterojunctions enable a new form of molecular bandgap engineering, as demonstrated by our scanning tunneling spectroscopy measurements. A current limitation of this technique, however, is that so far the structures can only be grown on metals. We are using scanned probe microscopy to explore new bottom-up synthesis routes that, in principle, should not be limited to metallic substrates.

**COLL 45**

**Direct observation of molecular monolayers on graphene/Au(111) at electrified interfaces**

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Graphene, a single carbon-atomic layer, is a fascinating material as an aromatic platform for chemical reactions. The π-π stacking interactions between graphene and aromatic molecules can form strong binding interactions, leading to atomic templating reactions for the molecular assembly. Here, we report electrochemical scanning tunneling microscopy (EC-STM) study for the molecular monolayers on graphene/Au(111) surfaces at electrified interfaces. Firstly, structural observations of variously layered graphene on Au(111) are investigated at different electrode potentials. For example, multilayer graphene shows superlattice structures due to interactions between graphene layers on the underlying reconstructed Au(111) structure. Secondly, we show influences of potential-induced structural changes of underlying Au(111) structures at observed graphene structures. Finally, in-situ molecular adsorption on graphene/Au(111) and their structural changes with respect to an electrode potential are investigated. The structures of molecular monolayers formed through the self-organization are determined by both the interactions of molecules with the graphene surface and the lateral interactions between the molecules. In particular, nanostructure formation can be generated from the diverse structures that result from electrode potential controlled self-assembly of molecules at electrified surfaces. Consequently, molecular nanostructures on graphene at liquid-solid interfaces are varied by the interplay between graphene-molecules, intermolecular, and graphene-underlying Au (111) surface interactions.

**COLL 46**

**Probing the origin of catalytic activity through scanning transmission electron microscopy and first-principles theory**

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Today's aberration-corrected scanning transmission electron microscope (STEM) allows direct, real space imaging at atomic resolution with low accelerating voltages to
minimize damage. Atom-by-atom characterization of atomic position, atomic species, chemical bonding and optical and electronic properties has become feasible. Furthermore, through direct momentum transfer, the STEM probe can also explore the dynamics of small clusters, revealing their energy landscape. Such capabilities allow unprecedented opportunities to unravel the origin of activity in a number of important catalytic systems. Examples will include the origin of nanopores and enhanced absorption in nanoporous carbons and the identification of single Nb atoms as sites of high activity with high stability in niobium–carbon catalyst for the cathodic oxygen reduction reaction in polymer electrolyte fuel cells. Finally, it will be shown how the STEM can be used to form transition metal chalcogenide nanowires from their respective dichalcogenide monolayer sheets. They are metallic, flexible, and self-healing against beam damage, making them attractive for interconnects in future flexible nano-circuits fabricated entirely within a monolayer.

In collaboration with Wu Zhou, Andrew R. Lupini, Junjie Guo, Matt Chisholm, Cristian I. Contescu, Nidia C. Gallego, Jaekwang Lee, Juan-Carlos Idrobo, Junhao Lin, Oak Ridge National Laboratory, Xuefeng Zhang, NRC Canada, Pengfei Guan, Johns Hopkins University and Sokrates T. Pantelides, Vanderbilt University.

**COLL 47**

**Magnetic resonance tool for observing the nanoscale hydration landscape**


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Over the past several years, we have been developing a technique capable of localized (5-10 Angstrom specificity) measurements of hydration dynamics that remains functional even for samples with high viscosity or low transparency. This technique, Overhauser Effect Dynamic Nuclear Polarization (ODNP), observes the dynamics of water nuclei that pass by a specially tethered electron spin label. ODNP has previously proven capable of measuring large changes in the dynamics of hydration water.

We first present an investigation of the hydration layer surrounding lipid vesicles in the gel phase. We find that water molecules in the hydration layer diffuse some 5.8 times slower than in the bulk. However, the diffusivity in the hydration layer remains unchanged even after a >10-fold increase in the bulk viscosity. We begin to see that interactions between the water and the surface appear to play a key, and sometimes overwhelming, role in determining the dynamics of the hydration layer(s).

We also examine GroEL/GroES, a chaperone system that forms a nanocavity to aid in the folding of certain proteins. We pair ODNP with a technique for probing local water density, and find remarkably bulk-like behavior of the water inside the nanocavity. Upon examining the surface of freely dissolved GroES, which is the "lid" of this nanocavity, we observe unusually fast dynamics that might help explain this unexpectedly bulk-like behavior.

COLL 48

Confocal Raman microscopy characterization of hybrid supported phospholipid bilayers in single C18-functionalized chromatographic particles

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Spectroscopic probing of lipid bilayers can provide insight into the structure and functioning of cell membranes and vesicles. Spectroscopic methods are challenged, however, by the sensitivity required to observe a small number (millions) of molecules in the lipid bilayer of a vesicle or planar supported bilayer. In the present work, this sensitivity challenge is met by depositing a model (hybrid) lipid bilayer on the interior surfaces of n-alkyl (C18) modified porous silica chromatographic particles. The highly porous silica provides a large surface area where the upper leaflet of DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine) forms a stable monolayer on the covalently bound C18-chains at the silica surface. The concentration of DMPC within a particle is sufficiently high to allow characterization of the hybrid bilayer using Raman microscopy. In this work, the structure and coverage of the hybrid bilayer acyl chains were determined using Raman scattering from C-C stretching modes of the surface bound C18 and upper-leaflet DMPC acyl chains. By spectroscopically monitoring acyl chain conformation versus temperature it was possible to observe the bilayer undergo both pre-transition and main-phase transition at 25.0 °C and 36.8 °C respectively; these are shifted to higher temperatures (shifts of ~10 °C for the pre-transition and ~12 °C for the
main transition) from the phase transitions of a DMPC vesicle membrane, in agreement with calorimetry results. To investigate the source of this temperature shift, Raman scattering from the lipid acyl chains was resolved from that of the surface C_{18} chains by using deuterated DMPC. From these results we conclude that both C_{18} and lipid acyl chains undergo simultaneous disordering as the bilayer passes through the two phase transitions, suggesting that the underlying, covalently-bound C_{18} chains stabilize the acyl-chain ordering of the upper-leaflet DMPC monolayer.

COLL 49

Enabling controlled positioning of analytes and cells on plasmonic sensors for surface enhanced spectroscopy: Where nanofabrication meets biology

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Plasmonic sensors are of particular interest to probe molecular species adsorbed on their surface, enhancing the sensitivity of spectroscopic measurements through the excitation of a localized surface plasmon. Advanced nano and microfabrication methods are keys to the development of such sensors allowing one to tailor optical fields at the subwavelength scale, hence optimizing excitation conditions to detect low concentration of analytes. Herein, a device has been developed based on a surface-modified micropatterning technique coupled with the arrays of plasmonic sensors with the goal to locate the analyte in a defined position onto the plasmonic sensor with the goal to perform surface enhanced measurements. The biocompatibility of the device has also been demonstrated highlighting the opportunity not only to isolate a given biological cell but also to probe biomolecules of interest within cells opening a new window on cellular chemical exchanges at a ultrasensitivity level.


COLL 50

Multiphoton microscopy optical imaging reveals many different structural features of fibrous collagen hydrogels in situ

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Collagen hydrogel microstructure depends on the protein solid content, incubation temperature, type and concentrations of ions as well as the pH. This paper will summarize our recent development of the multiphoton microscopy (MPM) optical imaging method to study the effect of these different physicochemical parameters on the micro-structural assembly of collagen within the three-dimensional (3D) hydrogels. The soft hydrated materials prepared have all been studied non-invasively and in situ. An interesting recent finding includes a strong potential of divalent anions to modulate the type of microstructure formed within collagen hydrogels. For example, in a phosphate-only buffer, when phosphate concentration is 30 mM, the fibers formed are about 1 μm in length as detected with second harmonic generation contrast (figure 1). Evidently, 60 mM phosphate induces an increase in the fibers’ length concomitantly leading to a micro-structural heterogeneity within the collagen hydrogel. A complete shift to about 45 μm fiber takes place when phosphate concentration is 160 mM. The pore size also increases from about 5 μm in the hydrogels formed at 30 mM phosphate to over 24 μm in the hydrogels formed at 160 mM phosphate. Adding 150 mM sodium chloride in a 30 mM phosphate buffer to polymerize collagen into a hydrogel at 37 °C does not lengthen collagen fibers. Our methods developed and the data obtained remove guesswork from engineering collagen-based materials for various applications.

Figure 1

Coll 51

Assembly of emulsion stabilizing agents at the liquid-liquid interface

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Emulsions made from oil/water mixtures are important for various industrial applications including food, cosmetic and pharmaceutical. Emulsions can be defined as being either oil droplets in water or water droplets in oil stabilized by molecular agents, such as surfactants, polymers or nano-materials. This study investigates the molecular characteristics of the commonly used surfactant AOT as it adsorbs at the oil/water interface of regular emulsions, reverse emulsions and the planar oil/water interface. The studies are a combination of vibrational sum frequency spectroscopy conducted in both a reflection and a scattering geometry with dynamic light scattering measurements. The studies provide new insights into how AOT plays a role in emulsion stabilization and the general characteristics of adsorption at the interface of two immiscible liquids.

**COLL 52**

**Bursting of elastic soap bubbles containing wormlike micelles**

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Slow-motion imaging of the rupture of soap bubbles generally shows the edges of liquid films retracting at a constant speed (known as the Taylor-Culick velocity). Here we investigate soap bubbles formed from simple solutions of a cationic surfactant (cetyltrimethylammonium bromide – CTAB) and sodium salicylate. The interaction of salicylate ions with CTAB leads to the formation of wormlike micelles (WLM), which yield a viscoelastic behavior to the liquid film of the bubble. The figure below shows the bursting dynamics as a function of salicylate mole fraction (ξ), demonstrating that these elastic bubbles collapse at a velocity up to thirty times higher than the Taylor-Culick limit, which has never been surpassed.
This occurs because during the bubble inflation, the entangled WLM chains stretch, storing elastic energy. This extra energy is then released during the rupture of the bubble, yielding an additional driving force for film retraction (besides surface tension). This new mechanism for the bursting of elastic bubbles may have important implications to the breakup of viscoelastic sprays in industrial applications.

**COLL 53**

**Drainage and stratification kinetics in foam films**

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Baking bread, brewing cappuccino, brushing teeth, pouring beer, washing dishes, shaving, shampooing, whipping eggs and blowing soap bubbles all involve creation of aqueous foam films. Foam lifetime, drainage kinetics and stability are strongly influenced by surfactant type (ionic vs non-ionic), and added proteins, particles or polymers modify typical responses. The rate at which fluid drains out from a foam film, i.e. drainage kinetics, is determined in the last stages primarily by molecular interactions and capillarity. Interestingly, for certain low molecular weight surfactants, colloids and polyelectrolyte-surfactant mixtures, a layered ordering of molecules, micelles or particles inside the foam films leads to a stepwise thinning phenomena called stratification. Though stratification is observed in many confined systems including foam films containing particles or polyelectrolytes, films containing globular proteins seem not to show this behavior. Using a Scheludko-type cell and interferometry, we experimentally study the drainage and stratification kinetics of horizontal foam films. Interference between light reflected from two surfactant-laden surfaces that are 100 nm - 10 micron apart leads to iridescent colors. Below 50 nm the thin films appear as black. We experimentally follow the drainage kinetics of foam films using imaging color science and UV-Visible spectroscopy. We find fascinating examples of two-dimensional hydrodynamics and unexplained, if not unprecedented, drainage kinetics.

**COLL 54**

**Nonlinear light scattering from droplets: Development of a versatile probe of aggregation and kinetics**

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Micelles, and emulsions are systems of fundamental importance to a wide range of industries including petroleum, food, and pharmaceutical. The need for surface sensitive techniques able to characterize colloids in situ and in a nondestructive way has recently contributed to the development of a new spectroscopic technique called nonlinear light
scattering. This technique has already been proven effective in probing properties and processes at the surface of solid colloidal particles in liquid and is, in this contribution, applied to study micelles and emulsions.

We have taken advantage of the interface sensitivity, size/shape-selectivity, and time resolution afforded by this technique to gain a fundamental understanding of the factors affecting the stability of emulsions and the formation and destruction of micelles: It is of paramount importance to be able to conduct such study in situ looking directly at the micelle/droplet surface instead of relying on indirect proofs. The effect of the molecular properties of the components, solvent characteristics, and environmental factors, such as pH and ionic strength, in affecting molecular aggregation and kinetics has been investigated and theories have been developed to explain the experimental observations.

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research.

**COLL 55**

**Nanostructuration of diblock copolymers at interface**

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Amphiphilic block copolymers are usually used as compatibilizer for polymers blends or as surfactant for emulsions. The organization and conformation of each block can be influenced by the interfacial interactions, especially if the blocks are able to crystallize. The objective of this work is focused on the effect of interface on the organization and crystallization of thin films of diblock copolymers deposited on model substrates.

Polyethylene-b-Polyethylene glycol (PE-b-PEG) diblock copolymers have been deposited on aluminum and model substrates (hydrophilic and hydrophobic surface obtained by a chemical grafting of a gold layer deposited on a silicon wafer). Each block is able to crystallize. PE block is apolar (hydrophobic character), while PEG block is polar (hydrophilic character). The aim is therefore to understand how the affinity of each block towards a given surface can govern the copolymer organization and crystallization. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) is used to characterize PE-b-PEG thin films, in order to get information about the organization of both blocks. These results will be compared with bulk analyses performed by Attenuated Total Reflection Infrared Spectroscopy (ATR) in order to evidence specific chains organization in thin films. Atomic Force Microscopy (AFM) analyses were also performed on thin polymer layer in order to characterize the morphology and nanostructuration.

Various PE-b-PEG copolymers (different compositions) have been deposited on substrates and studied by PM-IRRAS and AFM.
IR results have evidenced major differences in peaks intensities and positions between the thin films deposited on the various substrates.

Influence on chains organization of both substrate surface chemistry and copolymers composition will be discussed in terms of molecular orientations that can be probed by PM-IRRAS specific selection rules. AFM imaging will allow us to confirm the copolymers organization.

COLL 56

Preparation of double emulsions using hybrid polymer/silica particles: New Pickering emulsifiers with adjustable surface wettability

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A facile route for the preparation of water-in-oil-in-water (w/o/w) double emulsions is described for three model oils, namely n-dodecane, isopropyl myristate and isononyl isononanoate, using fumed silica particles coated with poly(ethylene imine) (PEI). The surface wettability of such hybrid PEI/silica particles can be systematically adjusted by (i) increasing the adsorbed amount of PEI and (ii) addition of 1-undecanal to the oil phase prior to homogenization. In the absence of this long-chain aldehyde, PEI/silica hybrid particles (1.0 wt % fumed silica, PEI/silica mass ratio = 0.50) produce o/w Pickering emulsions in all cases. On addition of sufficient 1-undecanal, this reagent reacts with the primary amine groups on the PEI chains, which renders the PEI/silica hybrid particles sufficiently hydrophobic to stabilize w/o Pickering emulsions at 20°C. ¹H NMR, gas chromatography and x-ray photoelectron spectroscopy provide compelling experimental evidence for this in situ Schiff base surface chemistry, while a significant increase in water contact angle indicates markedly greater surface hydrophobic character for the PEI/silica hybrid particles. However, when PEI/silica hybrid particles are prepared using a relatively low adsorbed amount of PEI (1.0 % w/w fumed silica, PEI/silica mass ratio = 0.075), the extent of surface modification achieved using this Schiff base chemistry is insufficient, and only o/w Pickering emulsions can be obtained. Fluorescence microscopy and laser diffraction studies confirm that highly stable w/o/w double emulsions can be achieved for all three model oils. Dye release studies from the internal aqueous cores into the aqueous continuous phase indicate some immediate loss of dye (12-18 %) during the high speed homogenization required for double emulsion formation, but no further dye release is observed at 20 °C for at least 15 days thereafter.

COLL 57

Surface and size effects on rheology of model nanoplatelets in epoxy
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The rheology and viscoelasticity of fluids and polymer melts containing dispersed particles are a bulk consequence of properties and processes that occur on length and time scales governed by the individual suspended particles. To clearly relate changes in macroscopic response to particle-level properties, and potentially higher-order levels of organization, explicit structure-property relationships between length scales are needed. We have investigated the linear and non-linear viscoelastic response of suspensions containing model 2-dimensional nanoparticles (nanoplatelets) over concentrations ranging from dilute to liquid crystalline. The particles are inorganic metal phosphates with α-zirconium phosphate (Zr(HPO\textsubscript{4})\textsubscript{2} \cdot H\textsubscript{2}O) structure and crystallize in stacks consisting of individual plate-like crystals. The shape, size, and exfoliation state of the nanoplatelets can be easily controlled based on reaction conditions and selection of surface modifier. The shape and size effects of the exfoliated nanoplatelets on the rheology of an uncured epoxy suspending fluid will be presented. The results show a rich range of rheological behaviors associated with a transition from Brownian to hydrodynamically dominated regimes. The steady shear response of the smaller nanoplatelets is consistent with the behavior of rigid Brownian plates. As aspect ratio increases, more complex phenomena such as double shear thinning and shear thickening are observed and attributed to a combination of particle-level effects, such as particle tumbling and deformation, and collective behaviors, such as the formation of aligned layers and transient stacks. The use of model nanoparticles with tunable shape and surface interactions allows a broad range of behaviors to be probed and meaningfully related to the motion and interaction of the individual particles.

COLL 58

Characterization of surfactant and nanoparticle stabilized concentrated emulsions using acoustic spectroscopy

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Concentrated emulsions have direct applications in the energy, food, agricultural, and pharmaceutical industries. Fundamental characterization of these systems is required to develop strategies that decrease the associated operating and treatment costs for managing these systems. This paper highlights the efforts underway at Oklahoma State University in using acoustic techniques for emulsion characterization, measurement of particle size distributions, and quantification of interfacial behavior for specific applications in the energy industry. Acoustic spectroscopy was chosen over other
particle characterization techniques due to its unique ability to characterize concentrated systems without dilution. The acoustic technique utilizes sound waves and the attenuation coefficient to characterize particle size, zeta potential, and conductivity. This work explores the morphology and transient behavior of both conventional surfactant stabilized and solid stabilized emulsions. This work utilizes several model oils and is coupled with inflow microscopy to quantify droplet size distributions. In this work, the behavior of a non-ionic surfactant and hydrophobic nanoparticle in stabilizing emulsion is investigated for both water-in-oil and oil-in-water emulsion types. Surface tension of select model systems will be presented through implementation of advanced interfacial tensiometry techniques. The drop size measurements coupled with surface rheology will lead to fundamental characterization of these concentrated emulsion systems.

COLL 59

Star diblock copolymer concentration dictates colloidal stability of carbon black particles in nonpolar media: Bridging flocculation vs. steric stabilization

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An AB diblock copolymer with a star-like architecture has been evaluated as a dispersant for carbon black particles, which serve as a model colloidal substrate. This copolymer comprises a major solvatophilic inner block and a minor solvatophobic outer block. It adsorbs onto the carbon black particles at ambient temperature and UV spectroscopy studies reveal a Langmuir-type isotherm via a supernatant depletion assay. This indirect analysis is corroborated by thermogravimetric analysis, which determines the actual amount of copolymer adsorbed onto the carbon black particles directly. At relatively low copolymer concentrations (i.e. below the knee of the adsorption isotherm) the carbon black particles become highly flocculated, as judged by optical microscopy and analytical centrifugation studies. Under these conditions, the copolymer acts as a bridging flocculant. At higher copolymer concentrations (i.e. above the knee of the isotherm), the carbon black particles become well-dispersed as a result of steric stabilization.

COLL 60

Modulating the arrangement of charged nanotubes by ionic strength in salty water

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Despite the important role and potential application of charged cylindrical polyelectrolytes, biomacromolecules, and self-assembles, salt-modulated organization
of those 1D charged nanostructures remains a topic relatively unexplored with an obscure underlying mechanism. In this Letter, the aggregation of oriented nanotubes self-assembled by ionic aromatic oligoamide in aqueous solution of NaCl over a wide concentration range is probed via small-angle X-ray scattering and transmission electron microscope. The arrangement of nanotubes undergoes order–disorder transition sequences from an ordered rectangular phase to hexagonal packing and then to a lamellar gel. The observed transitions are understood by ionic effects on the electrostatic interaction between charged nanotubes and osmotic pressure due to ion partitioning. Above the physiological condition, electrostatic interactions are largely screened by the salts, while osmotic effects start to regulate the aggregation behavior and concomitantly deform the nanotubes. The study demonstrates rich phase behaviors of ordered, charged 1D nanostructures by tuning the ionic strength and underlying key physical principles. Ref: Jiaojiao Tao+, Ningdong Huang+, et. al. the Journal of Physical Chemistry Letters (In press)

COLL 61

Use of an electric bottle for colloids to study phase transitions

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Particle concentration is an important factor that determines the phase behavior of all colloidal suspensions. We use electric field gradients to manipulate the local particle concentration in a suspension rather than gravity and temperature gradients. Combination of dielectrophoresis and confinement can give precise control over the particle concentration in a sealed sample cell. When the system comes to equilibrium under the action of electric field gradients, density gradients form naturally to counterbalance the electrostatic energy. It is possible to squeeze and relax particles by switching the electric field on and off respectively, which enables to study phase transformation processes such as crystal nucleation, growth, and melting.

**COLL 62**

**Colloidal stability and adsorption-driven self-assembly of ethyl cellulose nanoparticles at the air-water interface**

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Super stable foams have been recently generated from aqueous solutions of hydrophobic, charge-stabilized ethyl cellulose (EC) nanoparticles produced by a nanoprecipitation (anti-solvent) method. The exceptional stability of these foams has been broadly attributed to irreversible adsorption of EC nanoparticles at the gas-liquid interface, but the details of the adsorption process are not completely understood yet. We address in this work a number of fundamental questions related to nanoparticle-interactions controlling colloidal stability and nanoparticle-interface interactions during the course of EC nanoparticle adsorption. Using dynamic surface tension (DST) as a probe of EC nanoparticle adsorption, we show that irreversible adsorption kinetics is unequivocally characterized in terms of the adsorption energy and rate constant, and the maximum (jamming) coverage. Strong adsorption of EC nanoparticles is observed at neutral pH and in the absence of any ions, suggesting the parallel action of an attractive non-DLVO force. Consideration of a hydrophobic force explains strong adsorption for all ionic strengths and leads to quantitative predictions of colloidal stability. The former is revealed by the interpretation of DST measurements at different ionic strengths using a novel model. It is shown that the adsorption kinetics of EC nanoparticles are not affected by changes of the ionic strength, but colloidal stability is. Through a series of zeta-potential measurements and DLVO calculations, the transition from colloidal stability to coagulation with increasing ionic strength is defined. This transition is also determined experimentally by measuring the nanoparticle size distribution over time using dynamic light scattering and good agreement with theory is observed. These findings have significant implications for the fundamental understanding of colloidal systems and the utilization of nanoparticle colloids for the stabilization of emulsions and foams.

**COLL 63**

**Factors affecting the rate of PCET from reduced colloidal ZnO**
Charge transfer reactions at the interface of semi-conductor metal-oxides and solution play key roles in catalysis and energy conversion processes. Recent studies in our lab have shown that amine capped ZnO nanocrystals (NCs) dispersed in aprotic solvent are able to participate in proton-coupled electron transfer (PCET) reactions. Photolysis of anaerobic ZnO colloids leads to reduction and protonation of the NCs, by the oxidation of ethanol. These reduced and protonated NCs quantitatively and rapidly transfer protons and electrons to hydrogen atom acceptors.

We will present data from transient and stopped-flow UV-visible spectroscopy experiments that probe several factors that may affect the rate of PCET from these colloidal NCs. The importance of the nanoparticle size and therefore apparent reduction potential and the extent of nanoparticle reduction (the average number of electrons per NP) will be discussed. The effect of the concentration of the amine capping ligands and therefore the ligand surface coverage will also be described in this presentation.

**COLL 64**

**Understanding ligand-nanoparticle interactions to colloidal stability of silver nanoparticles**

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We perform a kinetic study of Ag nanoparticles (AgNP) using electrospray-differential mobility analysis (ES-DMA). Transmission electron microscopy (TEM) is employed orthogonally to provide imagery confirming primary size and also cluster state measured by ES-DMA. Distinct peaks (i.e., with different ion mobility) observed over a broad range of pH conditions represent different types of finite size nanoparticle clusters (e.g., dimers, trimers). For unconjugated AgNP, degree of aggregation is increased significantly with reaction time at pH<2.6. In comparison, particle size distributions and degree of aggregation are relatively unchanged at an acidic environment for bovine serum albumin (BSA)-conjugated AgNP. Based on the data of primary size measured by ES-DMA (i.e., the peak size of monomers) and TEM, the extent of AgNP dissolution is also evaluated together with the degree of aggregation. Combining information derived from ES-DMA, we can calculate the surface packing density of BSA on AgNP, aggregation rate constant, and stability ratios useful to estimate the shelf-life of AgNP-based products in dispersed form. Our results indicate aggregation is the dominant process for colloidal instability of AgNPs at the acidic pH range we study (pH>2.3), and BSA conjugation on the surface of AgNP can suppress the aggregation rate.
Coalescence behavior of giant Pickering droplets and colloidosomes stabilized by poly(tert-butylaminoethyl methacrylate) latexes

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The coalescence of two millimeter-sized n-dodecane droplets grown at pH 10 in the presence of lightly cross-linked 260 nm diameter charge-stabilized poly(tert-butylamino)ethyl methacrylate (PTBAEMA) latexes was monitored using a high-speed video camera. n-Dodecane was investigated as an oil phase in the absence and presence of an oil-soluble cross-linker (tolylene 2,4-diisocyanate-terminated poly(propylene glycol), PPG-TDI). In the absence of PPG-TDI, rapid coalescence was observed for giant PTBAEMA-stabilized Pickering oil droplets. An increase in the damping coefficient for coalescing PTBAEMA-stabilized n-dodecane droplets (compared to that for bare oil droplets) indicated PTBAEMA latex adsorption at pH 10. Addition of PPG-TDI cross-linker to the oil droplets led to a reduction in the interfacial tension, confirming the surface-active nature of this reagent. PPG-TDI was added to the oil phase to react with the secondary amine groups on the PTBAEMA latex, producing giant colloidosomes that were stable to coalescence when brought into contact. This was not observed for bare oil droplets in the presence of PPG-TDI, confirming that the cross-linked latex particles at the interface provide the additional stability towards coalescence. Separation of the colloidosomes five minutes after their contact produced a visible ‘neck’ connecting the droplets. Subsequent separation of the n-dodecane-based colloidosomes merely stretched the interfacial contact area, indicating formation of inter-crosslinked colloidosomes. Asymmetric interactions between a Pickering droplet and a colloidosome were also examined. The effect of adding PPG-TDI cross-linker to only one droplet resulted in “arrested coalescence” behaviour in the presence of PTBAEMA latex particles at pH 10. In this context, the droplet aging time was found to be critical. Aging times of less than 60 s led to droplet coalescence, whereas aging times longer than 60 s indicated cross-linker diffusion from one droplet to the other, which produced inter-crosslinked colloidosomes. Arrested coalescence was only observed for intermediate aging times of approximately 60 s.

Surfactant-mineral interactions with applications in oil-spill dispersion and clean-up
We consider silica nanoparticles in terms of their ability to disperse oil in water. The surface properties of silica are modified by a change in the solution pH and/or the adsorption on the surface of surfactants of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) family. The physical adsorption of surfactant polymers, and corresponding interactions between silica nanoparticles, can be modulated by the addition of displacers such as polar organic solvents, PEO homopolymers, or electrolytes. The connection that we establish between (a) the surfactant organization on the nanoparticle surface and in the bulk solution and (b) macroscopic properties of the dispersions can guide the design of oil-in-water dispersants that incorporate environmentally benign nanoparticles.

COLL 67

Surface water fluctuations and chemical reactivity at liquid/liquid interfaces

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The rate of a chemical reaction with a significant variation of the reactants' charge distribution along the reaction coordinate is strongly dependent on solvent polarity. When this reaction take place at the oil/water interface, coupling of the reaction coordinate to water surface fluctuations produces unique dependence of the rate on reactants location and orientation. We demonstrate this behavior by examining a series of reactions such as ion-pairing, nucleophilic substitution and proton transfer.

COLL 68

Wetting of hydrophobic spaces by hydrated excess protons

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The Grotthuss hopping mechanism for the hydrated excess proton, which is the process of the net positive charge defect translocation via the rearrangement of the covalent bonds, is the key to interpreting many unique characteristics of proton transport in aqueous systems. For many years, Grotthuss proton transport through hydrogen bonded water networks has been the focus of theoretical and experimental discussions. However, is there a related process in which water can be transported through a proton charge defect in order to "wet" the "path ahead" for the charge defect to then migrate? This process has been recently observed in our computer simulations of explicit proton transport through a hydrophobic carbon nanotube. A 30 Å dry nanotube was assembled between two graphene sheets separating bulk water. Surprisingly, before the hydrated
proton enters the tube, it starts shuttling water molecules into the otherwise dry tube via Grotthuss shuttling, effectively creating its own water wire where none existed before. As the proton enters the nanotube (2\sim 3 \text{ Å} in), the tube transitions to being fully wet. Water molecules enter the nanotube by passing “through” the proton charge defect via the Grotthuss-like bonding topology rearrangement. Interestingly, other monoatomic cations (e.g., K+) have just the opposite effect - blocking the wetting process and making the nanotube even drier. As the dry nanotube gradually becomes wet when the proton charge defect enters it, the free energy barrier of proton permeation through the tube drops significantly. This finding suggests that an important wetting mechanism may influence proton translocation in biomolecular systems, one in which protons “create” their own water structures in hydrophobic spaces (e.g., protein cavities) before migrating through them. If this is true, then a prior existing “water wire”, e.g., one seen in an x-ray crystal structure or molecular dynamics simulations without an explicit excess proton, may not be necessary for excess protons to transport through hydrophobic spaces via water mediated Grotthuss shuttling. They can create their own water wires as needed.

**COLL 69**

**Structure and dynamics of water in nanopores**

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This presentation will focus on our molecular simulation results for the structure and dynamics of water confined in approximately cylindrical pores with diameters ranging from 20 to 40 Å. The primary focus of our work is on porous amorphous silica, resembling MCM-41 materials. Other model pores are also investigated in order to determine the effects of surface roughness and hydrophilicity. We use Gibbs ensemble Monte Carlo simulation to prepare fully hydrated pores and then molecular dynamics simulation to calculate water structure and dynamics. Our results for water in silica pores indicate that water forms two distinct molecular layers at the interface and exhibits uniform, but somewhat lower than bulk liquid, density in the core region. The hydrogen bond density profile follows similar trends, with lower than bulk density in the core and enhancements at the interface, due to hydrogen bonds between water and surface non-bridging oxygens and OH groups. Our initial characterization of water dynamics included translational mean squared displacements, orientational time correlations, survival probabilities in interfacial shells and hydrogen bond population relaxation. We found that the radial-axial anisotropy in translational motion largely follows the predictions of a model of free diffusion in a cylinder. However, both translational and rotational water mobilities are strongly dependent on the proximity to the interface, with pronounced slowdown in layers near the interface. In order to make contact with experiments on water dynamics within the pores, we have calculated and analyzed the self-intermediate scattering function (ISF) of water hydrogens, the observable in quasi-elastic neutron scattering (QENS) and the collective polarizability anisotropy time
correlation, measured in optical Kerr effect (OKE) experiments. Our findings on the dynamics of confined water detectable by QENS and OKE will be discussed.

**COLL 70**

**Molecular simulations of water in clay mineral nanopores**

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The molecular simulation of water in confined geometries has been an abiding theme of Jay Rasaiah's research. These simulations not only visualize molecular scale structure, but also inform interfacial molecular spectroscopy, exploring structural details experiment cannot fully resolve, while providing tests of the assumptions underlying predictive models of interfacial chemistry. This approach will be illustrated through our own recent studies of water in the interlayer nanopores of clay minerals (smectites), which are highly-reactive layer type nanoparticles found in natural earth materials and environmental barriers. We report detailed molecular dynamics simulations elucidating the structure of water and the electrical double layer near smectite siloxane surfaces, which possess both hydrophilic sites and hydrophobic patches, then use our results to examine a surface complexation model widely used to describe cation adsorption by the hydrophilic sites. Finally, we preview our very recent results using methane as a probe of the hydrophobic patches on siloxane surfaces.

**COLL 71**

**Pressure and electric field induced superhydrophobic transitions: Reversibility and dynamics**

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The fluid flow control at the nanoscale represents a great challenge for the design of lab-on-a-chip devices and manipulation of nanodroplets. The exploit of superhydrophobic surfaces, where the surface and the water interfaces are separated by air trapped between pillars (Cassie state), could represent a promising way to increase or decrease the friction of a fluid on a channel walls by controlling the presence of the air layer. The well known metastability of the Cassie state with respect to the air-free system (Wenzel state) however is a big obstacle in achieving a reversible control of the two contrasting wetting states. The reversibility could be restored by reducing the length scale of corrugation down to nanoscale. We use molecular dynamics simulations to investigate the reversibility of a submerged model surface with sub-nanometer roughness promoted by two different driving forces,
pressure and electric field. In both scenarios we observe fast (O(sub-ns)) unlimited cycling between the two states, the associated hysteresis being due to the nucleation of a vapor bubble between the pillars during the Wenzel to Cassie transition. We also investigate cooperative effects between water densities in neighboring inter-pillar sites to get a deeper insight into the similarities and differences between the pressure and electric field induced transitions.

COLL 72

**Water permeation, desalination, gating, and dipole signal transduction with nanopores**

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Several water nanopores, including single-wall carbon nanotube (SWNT), Y-shaped carbon nanotube (Y-CNT), nanoporous 2D Fe phthalocyanine (FePc), have been studied with large scale molecular dynamics simulations on their capability in water permeation, desalination, gating and even signal transduction. The water permeation across a SWNT can be controlled with a single electron/proton. The effect on the water flow and net flux in the confined nanotube is found to be negligible when the external charge of value is beyond a critical distance from the wall of the SWNT. This designed nanopore shows an excellent on-off gating behavior by a single charge. Meanwhile, one signal at single-electron level can be converted and multiplied into two or more stable signals by water chains confined in a narrow Y-CNT. This remarkable transduction capability of molecular signal by Y-CNT is found to be attributable to the surprisingly strong dipole-induced ordering of such water chains, such that the concerted water orientations in the two branches of the Y-CNT can be modulated by the water orientation in the main channel. The response to the switching of the charge signal is very rapid, from a few nanoseconds to a few hundred nanoseconds. As for the FePc nanopore, interestingly, we find that it not only conducts fast water flow, with a water conductivity up to 6.5 L/cm²/day/MPa, but also can fully exclude the permeation of Na⁺ ions, and also limit the Cl⁻ ions’ transduction rate to be four orders of magnitude smaller than water. Such remarkable selectivity is attributed to the unique feature of FePc nanopores which is distinct from traditional steric exclusion mechanism. In addition, the number of protonated nitrogen atoms in FePc pores can be modulated by adjusting the pH value of the solution. The extent of the anion trapping and occupancy can thus be regulated, giving rise to the control of the water flow.

COLL 73

**Nanofiber and nanotube-enabled water treatment technologies: Reactivity and fate studies**
Engineered nanomaterials represent a promising but as yet untapped resource for development of advanced water treatment technologies. Here, we present ongoing work from our laboratory on the performance of carbon nanotube and reactive nanofiber technologies. Carbon nanotubes are utilized as reactive substrates during ozonation for hydroxyl radical production, while various form of reactive nanofibers synthesized via electrospinning are utilized as photocatalysts and sorbents. In addition to reactivity studies establishing their promise in chemical treatment processes, this talk will also emphasize material characterization and fate during their application as reactive coatings on membrane supports. To ensure responsible environmental application of nanomaterials, we consider their stability and transformation as a function of their performance lifetime in simulated water treatment applications.

**COLL 74**

**Applications of surface absorbing nano-size polymer colloids at The Dow Chemical Company**

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Over the last 50+ years The Dow Chemical Company has had numerous research programs involving the preparation and use of nano-size colloidal systems. The nano-colloids used range from soft (liquid microemulsions) to solid (polymeric) materials and from organic to inorganic. Application areas include catalysis, polymer latexes, delivery systems, consumer and personal care products, reaction media and nanoporous materials. In this presentation we will give an overview of the impact of nano-colloids at Dow and how we have utilized surface absorbing nano-colloids in a variety of applications. We will also describe in detail two application areas- Synthesis of nano-sized polymer colloids and their use in the preparation of nanoporous polymer films and use of nanoparticles as delivery systems in Agricultural applications.

**COLL 75**

**How well do carbon nanotubes and other nanoparticles stick to graphene?**

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This talk describes computational studies and related experiments aimed at determining the adhesion of carbon nanotubes and other nanoparticles to graphene on a copper
substrate. The primary focus of this work is an experiment in Horacio Espinosa's lab in which MWCNT’s are peeled from graphene, where the modeling studies consider such factors as the collapse of CNT's on a surface, and the role of graphitic flakes that are always present in such experiments on the mechanical measurements. A second study is concerned with the formation of ZnO nanoparticles on graphene using ALD.

COLL 76

Interactions of graphene oxide with model cell membranes

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Graphene is a two-dimensional, carbon-based nanomaterial with unique electrical, mechanical, and thermal properties. Graphene oxide (GO) is the oxidized form of graphene. Several recent studies have provided evidence that GO can exhibit toxicity toward human cells and bacteria. The studies also showed that GO can damage cell membranes. The mechanisms for the disruption of cell membranes by GO, however, are still not well understood. The objective of this study is to investigate the interactions between GO and model cell membranes in order to better understand the mechanisms for the cytotoxicity of GO. In this study, supported lipid bilayers (SLBs) composed of zwitterionic 1,2-dioleoyl-sn-glyero-3-phosphocholine (DOPC), as well as DOPC vesicles, are used as model cell membranes. The deposition rates of GO on SLBs are measured with a quartz crystal microbalance with dissipation monitoring (QCM-D). The deposition kinetics are shown to increase with increasing salt (NaCl or CaCl₂) concentrations under neutral pH conditions, indicating that electrostatic interactions are likely to play a critical role in controlling the attachment of GO to cell membranes. When GO comes into contact with DOPC vesicles, no significant damage to the vesicles is observed. Further investigation will be conducted with the use of a fluorescent dye to evaluate the integrity of vesicles when GO attaches to the cell membranes.

COLL 77

Environmentally relevant properties of polymer-carbon nanotube composites

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One of the most important commercial applications of carbon nanotubes (CNTs) involves their incorporation into polymer matrices to improve thermal, mechanical, and electrical properties. Indeed, most engineered nanomaterials, such as carbon nanotubes (CNTs) will enter the environment within nanoproducts, such as polymer nanocomposites. In this presentation I will discuss several environmentally relevant properties of polymer-CNT composites, including:
(1) Impact of CNT inclusion on biodegradation properties: Polymer nanocomposites will often be exposed to microorganisms when they enter the environment post-consumer. The effect of embedded CNTs on microbial interactions and polymer biodegradation rates will be discussed.

(2) Quantifying CNT release rates: From a life cycle perspective, determining CNT release rates is important in terms of risk assessment, because release is the precursor to exposure. However, a major challenge is the need to accurately detect and quantify released CNTs under environmentally relevant conditions where CNT concentrations are expected to be at part-per-trillion levels. Due to the ambiguities inherent in detecting CNTs by carbon analysis, particularly in complex environmental matrices, we been exploring the possibility of using single particle – inductively coupled plasma – mass spectrometry to detect trace catalytic metal nanoparticles intercalated in the CNT structure as proxies for the nanotubes.

(3) Effect of CNTs on polymer photodegradation properties: One of the principle routes of polymer degradation in the environment is through photodegradation. We have focused on the photodegradation behavior of CNT-nanocomposites with a focus on understanding how the presence of CNTs influence the mechanism and kinetics of photodegradation as well as the extent to which CNTs are released into the environment during the photodegradation processes.

Collectively, this information has important consequences in assessing the environmental risks posed by polymer-CNT nanocomposites, in developing better risk assessment models and the design of nano-enabled products that retain their intended function without posing any unwanted long-term environmental liability.

**COLL 78**

**Interaction of carbon nanotubes and graphene nanoplatelets with wastewater biomass**

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Municipal sewage and wastewater treatment plants (WWTPs) have been identified as primary vectors for conveying nanomaterials from industrial processing and consumer use of nano-enabled products. Building upon our previously developed methodologies to study wastewater biomass interaction with C60 and metallic nanoparticles and their removal in WWTP, we have developed extraction and analytical methods capable of quantifying CNTs, graphene nanoplatelet (GNP), or graphene oxide (GO) materials in
the presence of cellular materials. We describe the digestion of these cellular materials, through examples with biomass and lung tissue. Experimental results using these methods with wastewater biomass and a wide array of CNTs, GNP, GO is presented. The data is interpreted based upon principles of mechanisms that occur at the interface of nanomaterials and biomass.

Photochemistry and photobiological implications of functionalized fullerenes in aqueous systems

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Fullerenes have been the focus of significant research effort and curiosity for their unique physicochemical and photochemical properties since their discovery almost 30 years ago. C₆₀ fullerene in particular has received tremendous attention, due to its prevalence in fullerene production and chemical stability. While ambitious prospective applications for C₆₀ have been ubiquitous, the extremely hydrophobic nature of fullerenes and consequent aggregation at the nano scale has hampered many endeavors. Researchers, therefore, have turned their attention to the functionalization of fullerenes to add hydrophilic moieties for applications in aqueous media. It is known that functionalizing the C₆₀ cage alters its innate physicochemical and photochemical properties, but how these changes translate to the properties of C₆₀ aggregates, often termed nC₆₀, is not well understood. Functionalized fullerenes present an intriguing environmental dichotomy. On the one hand C₆₀ has excellent potential as a novel singlet oxygen (¹O₂) producing disinfection tool, and on the other the potential toxicological effects of functionalized C₆₀ are largely unknown. With thousands of possible functionalities, a mechanistic understanding of the effects of functionalization is essential.

To explore the effects of functionalization on fullerene photochemistry in relevant systems, three types of functional groups were selected and obtained each in series of mono-, bis-, and tris-functionalized forms. Two functionalities contrasted the presence or lack of a quaternary ammonium group and the third was the sterically bulkier phenyl-C₆₁ butyic acid methylester (PCBM), which is commonly used in polymer photovoltaics. The fullerenes were characterized for innate photochemical properties in organic solvents using UV/Vis, laser flash photolysis, and photochemical degradation experiments. Aqueous aggregates of each derivative were prepared via a sonication method and subjected to the same protocols with additional characterization of their physical and chemical properties by dynamic light scattering, transmission electron microscopy, energy dispersive x-ray spectroscopy, and x-ray photoelectron spectroscopy. All derivatives were found to be similarly photoactive when dispersed molecularly in organic solvents, but only the cationic fullerenes showed significant
photoactivity as aqueous aggregates. Differences in aggregate size or crystallinity were unable to explain the differential photoactivity between derivatives, contrary to two established hypotheses. Antimicrobial properties were probed using innate toxicity tests and photoinactivation experiments. Again, only the cationic fullerenes were found to exert photochemical action towards *Escherichia coli* or MS2 bacteriophages. The cationic fullerenes were also innately toxic to *E. coli* due to the presence of quaternary ammonium moieties.

In order to establish a mechanistic understanding of the photochemistry of functionalized C$_{60}$ aggregates, simulations of the molecular dynamics (MD) were employed and compared with empirical evidences. Simulations provided theoretical values for C$_{60}$-O$_2$, C$_{60}$-C$_{60}$, and C$_{60}$-H$_2$O interactions for each derivative. Additional computational characterizations of hydration structure were performed. Trends observed in the MD results were compared to photochemical characterizations as described above and from the following techniques used to probe changes water lattice structure: Raman spectroscopy, calorimetric analyses, and contact angle measurements. These observations collectively suggest that fullerene aggregate photochemistry is driven more by the intermolecular interactions between fullerenes, water, and O$_2$ than by the size or crystallinity of aggregates.

**COLL 80**

**Production of rhamnolipids from unique pseudomonads**

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The promise of biosurfactants has a long and storied history of having commercial potential. One of the major classes of biosurfactants is glycolipids that have the potential to replace a number of petroleum based surfactants due their sulfate and phosphate free nature while having superior surfactant properties. This class of glycolipids are characterized by either a mono or di rhamnose head group and a 3-((hydroxyalkanoyloxy)alkanoic acid tail that varies in molecular weight according to a number of factors including feedstock, fermentation time and Pseudomonas strain. Logos Technologies has developed three strains of Pseudomonads that produce rhamnolipids at high titers.

In this presentation, Logos Technologies will discuss the three strains of Pseudomonads that have been isolated for the overproduction of both mono- and di-rhamnolipids. Each strain has a unique rhamnolipid molecular weight profile for a specific feedstock. Results will be presented discussing how these two variables interact. In addition, the rhamnolipids need to be isolated from the fermentation broth for utilization. Data demonstrating a correlation between the molecular weight distribution of the rhamnolipid isolates and the CMC will be presented. These biosurfactants have the
characteristics and can meet the cost targets necessary for large scale commercialization.

COLL 81

Bactericidal activity of controlled-release antimicrobial chlorine dioxide

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The World Health Organization (WHO) reports diseases caused by airborne pathogens (i.e., tuberculosis, lower respiratory infections and pulmonary diseases) account for more than 10 million deaths each year. In 2002-2003, airborne droplets rapidly spread coronavirus resulting in the large community outbreak of the Severe Acute Respiratory Syndrome (SARS) in Hong Kong and other countries. Bioaerosol is also the key transmission route for the spread of H1N1 influenza virus during the recent global pandemic in 2009. Contrary to earlier belief, microorganisms are shown to survive and persist as bioaerosols. This is particularly worrying as many airborne pathogens are viable but not cultivable leading to severe underestimation of their potential risk to individual and public health.

This work reports on a new multilevel antimicrobial system based on the controlled-release of a gaseous biocide, chlorine dioxide for “release-killing” properties. “Contact-killing” and “anti-adhesion properties” were engineered on the encapsulating shell using a catalytic-dyad and detergent polymer. The antimicrobial system was incorporated into two types of particulate air filter (i.e., HVAC and HEPA). The “release-killing”, “contact-killing”, and “anti-adhesion” properties of the new multilevel antimicrobial particulate air filters were investigated separately for their effectiveness against Gram-positive and Gram-negative bacteria, bacteria endospores and fungal spores. Better than 2 log reduction was achieved in 10 min contact with the filter and accelerated life test indicated that an operation life of at least 12 months. Microscopy, spectroscopy and bioassay studies show that the predominant cause of microbial inactivation is through ROS route with cell wall peroxidation.

COLL 82

DNA-mediated surface reactions for nanostructure fabrication

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DNA nanostructures are ideal templates for nanoscale fabrication. However, their low chemical stability has been a major challenge in their applications in this area. This talk will present our recent advance in using DNA to modulate surface reactions. Based on these reactions, we have demonstrated high resolution (<10 nm), high throughput pattern transfer from DNA to a wide range of organic and inorganic materials, including SiO₂, Si, and silane self-assembled monolayers.

COLL 83

Stable archaean lipid-inspired biomaterials

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Archaea are a domain of prokaryotes that are most widely recognized for surviving in harsh environmental conditions such as high salinity, acidic or alkaline pH, very low or high temperatures and high pressures. Their ability to thrive in these harsh conditions is attributed to the increased stability of their lipid membranes, which are composed of lipids containing fully saturated phytanyl alkyl chains connected through ether bonds to the glycerol backbone, compared to regular lipid membranes composed of phospholipids. These features increase the rigidity and robustness of their membranes resulting in a reduced permeability to ions and small molecules. These properties of archaeal lipids, along with their potential to be interfaced with biomolecules presents an attractive platform for the generation of stable, programmable, stimuli-responsive liposomes, capable of ion/small molecule encapsulation and their subsequent controlled release. Herein, we focus our efforts on improving and developing stable systems via the design, synthesis and characterization of novel Archaeal-type lipids for the formulation of new stable programmable materials.

COLL 84

Structural analysis of the protofilaments as units of amyloid fibril by SAXS

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Amyloid fibril is one of the causative agents of Alzheimer's disease and its structure and amyloidosis behavior is a major interesting of the researchers. Some kinds of protofilaments are precursors of the amyloid fibril, and they were usually made with oligo peptides. The structure and physical properties of the protofilaments should be related with amyloid forming, and its fundamental study should lead to reveal the amyloidosis behavior. We prepared 2 model peptides for the unit of proto filament. They
had a part of Ovalbumin sequence that could form β-sheet structure, and one of them was combined with polyethylene glycol and the other was combined with TAT sequence. We carried out CD measurements, and we found the protofilaments contained β-sheet structure, that means the protofilament also took laminated structure as same as general amyloid fibril did. From the study of the X-ray scattering, the protofilaments took rod-like shape, and we found its cross section was rectangular shape rather than round shape (see figure 1, solid line shows theoretical curve of the rectangular rods). That is reasonable for the laminated structure of β-Sheets, and the layer number was calculated as 4 from the width of the rectangle.

**COLL 85**

**Phase transitions in antibody solutions: From pharmaceuticals to human disease**

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Antibodies are very important proteins. Natural antibodies play essential role in the immune system of human body. Pharmaceutical antibodies are used as drugs. Antibodies are also indispensable tools in biomedical research and diagnostics. Recently, a number of observations of phase transitions of pharmaceutical antibodies have been reported. These phase transitions are undesirable from the perspective of colloid stability of drug solutions in processing and storage, but can be used for protein purification, X-ray crystallography, and improving pharmokinetics of drugs. Phase transitions of antibodies can also take place in human body, particularly in multiple myeloma patients who overproduce monoclonal antibodies. These antibodies, in some
cases, crystallize at body temperature and cause severe complications called cryoglobulinemia.

I will present the results of our current studies on phase transitions of both pharmaceutical antibodies and cryoglobulinemia-associated antibodies. These studies have shown that different antibodies have different propensity to undergo phase transitions, but their phase behavior has universal features which are remarkably different from those of spherical proteins. I will discuss how studies of phase behavior can be useful in assessing colloid stability of pharmaceutical antibodies and in early diagnostics of cryoglobulinemia, as well as general implications of the fact that some antibodies can precipitate at physiological conditions.

**COLL 86**

**Nanocrystalline ordering in protein gel beads**

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Protein solutions exhibit a metastable liquid-liquid phase transition, similar to that observed for short-ranged colloids. Like short-ranged colloids, dynamical arrest of protein solutions within the two-phase region can lead to amorphous dense phases such as gels and precipitate particles. Due to their complex surface chemistry, proteins do not interact in a centro-symmetric fashion. Therefore, much effort has been made to calculate “patchy” colloid phase behavior and apply these models to protein solution phase behavior. A key to testing these predictions and to guide further study is characterization of the microstructure of protein dense phases. In this study, we use small-angle scattering techniques and real-space imaging to explore the microstructure of a model protein system, ovalbumin. Transmission electron microscopy (TEM) shows that macroscopically non-crystalline ovalbumin precipitate particles formed under high salt conditions (> 2.4 M ammonium sulfate) exhibit a particle-spanning network of aggregated protein with network branches having thickness 10-20 nm. Small-angle neutron scattering (SANS) measurements show that the particles exhibit a microstructure that at small length scales can be described by a 14 by 19 by 42 nm nanocrystalline cluster made up of 30 ovalbumin unit cells. At larger length scales, SANS exhibits a peak corresponding to characteristic spacing between branches of the network observed in TEM. In addition to the structural information, we find that the emergence of the microstructure depends on the quench depth into the spinodal, with shallow quenches resulting in faster microstructure development. These kinetic observations can be related to results of simulations previously reported in the literature.

**COLL 87**

**Crystallization of micrometer sized colloids with DNA hybridization**
We demonstrate a general approach to functionalize micrometer sized colloidal particles with oligonucleotide (DNA). Using strain-promoted alkyne-azide cycloadditions (SPAAC), particles with dense, stable and evenly distributed DNA are obtained. The resulting colloidal particles can self-assembled into crystalline structures mediated by DNA hybridization. Polystyrene and TPM (methacrylate silica hybrid) based particles are shown as examples. The particle surface is first functionalized with azide, and then allowed to conjugate with dibenzocyclooctyne (DBCO) modified DNA with sticky ends. The strategy is selective toward functional groups and surface chemistry, enabling the site-specific functionalization of patchy particles. Our effort toward crystallization of such particles will also be demonstrated.
We theoretically investigate and quantify the effects of pH and salt concentration on the charge regulation of the bacteriophage PP7 capsid. These effects are found to be extremely important and substantial, introducing qualitative changes in the charge state of the capsid such as a transition from net-positive to net-negative charge depending on the solution pH. The overall charge of the virus capsid arises as a consequence of a complicated balance between the chemical dissociation equilibrium of the amino acids, the electrostatic interaction between them and translational entropy of the mobile solution ions, i.e., counter ion release. We show that in order to properly describe and predict the charging equilibrium of viral capsids in general, one needs to include molecular details as exemplified by the acid-base equilibrium of the detailed distribution of amino acids in the proteinaceous capsid shell.

**COLL 89**

**Real time AFM study of kinetics of biomolecule assembly onto DNA nanostructure**

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DNA or RNA aptamers and biotin have become standard tools in nanobiotechnology, used for binding molecules or forming links between molecules. These simple modifications enable high-resolution placement of a variety of other species, including various biologically relevant molecules, metal nanoparticles, quantum dots, and carbon nanotubes onto DNA Origami structures. As DNA nanotechnology evolves many issues related to manufacturability will necessarily be raised, including kinetics of assembly. In this study, the technique of "real time" AFM was employed to evaluate the kinetics of assembly of streptavidin (SA) onto extended 1 dimensional arrays of cross-like origami constructs bound to a mica surface. As demonstrated in Fig. 1, this high speed imaging study revealed that, under the experimental conditions employed, assembly was essentially complete in less than 16 seconds. The AFM imaging system was operated at 0.4 sec/frame, far below its maximum scan rate. We shall also report on a similar study of the kinetics of self-assembly onto a DNA based array.
Anthropogenic pollutants enhance secondary organic aerosol production from the heterogeneous chemistry of isoprene-derived epoxides: Implications for air quality, climate, and public health in the southeastern U.S.

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Isoprene is a major source of secondary organic aerosol (SOA). Improving our fundamental understanding of isoprene-derived SOA is key to improving existing air quality models, especially since these models currently underestimate observations. By combining organic synthesis, computational calculations, mass spectrometry, smog chamber studies, flow tube studies and field measurements, we show that reactive epoxides, which include methacrylic acid epoxide (MAE) and isomeric isoprene epoxydiols (IEPOX), produced from the atmospheric oxidation of isoprene are key to SOA formation. Furthermore, anthropogenic pollutants enhance these epoxides as an SOA source. In the laboratory, we find that the reactive uptake of synthetic IEPOX and MAE standards onto acidified sulfate aerosol yields known isoprene-derived SOA tracers (2-methyltetrols, 2-methylglyceric acid, C₅-alkene triols, 3-methyltetrahydrofuran-
3,4-diols, dimers and organosulfates) that we measure in fine aerosol collected from multiple sites across the southeastern U.S. using gas chromatography/mass spectrometry (GC/MS) and liquid chromatography coupled to diode array detection and electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (LC/DAD-ESI-QTOFMS). Notably, IEPOX- and MAE-derived SOA molecular tracers account for a significant mass fraction (10-20%) of ambient OA. Moreover, real-time continuous chemical measurements of fine aerosol made using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) during summer 2011 and 2013 resolved IEPOX-derived SOA when applying positive matrix factorization (PMF) to the organic mass spectral time series. IEPOX-derived SOA is found to account for upwards of 33% of the fine OA mass and is correlated with known molecular tracers, sulfate, and aerosol acidity. We have investigated the heterogeneous kinetics of MAE and trans-b-IEPOX. The reaction probability, also called the reactive uptake coefficient, is calculated for MAE and IEPOX on 1-2 component aerosol particles under various aerosol compositions and environmental conditions in order to probe the chemical drivers of the epoxide uptake. New findings on how this chemistry impacts climate and public health will also be discussed.

COLL 91

Physical characterization of real urban grime

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When impervious surfaces are exposed to the atmosphere, surface films forms through the deposition, partitioning and subsequent processing of atmospheric constituents. There is evidence suggesting that these films, referred to as grime, play a role in mediating organic contaminants in the atmosphere and more recently we have shown that they provide a photo-reactive environment for the formation NOₓ from HNO₃ and possibly organic nitrogen species within the film. These reactive processes are enhanced in the presence of water vapour. We will present the results of quartz crystal microbalance measurements of the water uptake onto field-collected urban grime as well as an examination of film properties that may mediate this uptake. Using ATR spectroscopy, we probe the overall chemical and optic features of the grime samples; ion composition is measured using ion chromatography. We will report on how these evolve over multiple week sampling periods and different atmospheric and weather conditions.

COLL 92

Modeling the transport of chemical warfare agents and simulants in polymeric substrates to predict vapor exposures

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Polymer systems can absorb and subsequently reemit various toxic chemicals as a vapor. This is a significant challenge for polymers exposed to chemical warfare agents that people may interact with after contamination. The absorption and vapor emission processes are specific to the chemistry of the chemical and polymer systems. Chemical warfare agent simulants are often used for environmental testing in place of the highly toxic agents. Therefore, there is a need to understand the relationships across chemicals for transport into and out of materials. To prevent negative health effects resulting from exposure to the chemicals emitted by these polymers into the atmosphere, there is also a need to understand the decontamination of these chemicals from polymers. To reduce exposure, the decontaminant must access the absorbed chemicals and consider the surface and subsurface transport and reactivity. This work sets the foundation for modeling liquid-phase decontamination of absorbing polymeric materials with the focus on determining relationships between agents and simulants. The correlations of agents to simulants must consider the three way interactions in the chemical-material-decontaminant system where transport and reaction occur in polymer materials. To this end, diffusion modeling of the subsurface transport of simulants (e.g., chloroethyl phenyl sulfide, methyl salicylate) and live chemical warfare agents (e.g., Bis (2-chloroethyl) sulfide [mustard gas], O-ethyl S-[2-(diisopropyl- amino)ethyl] methylphosphonothioate [VX], and O-Pinacolyl methyl-phosphonofluoridate [soman]) was conducted for various polymer systems (e.g., polyurethane paint coatings, silicone elastomers). The models utilized 1D and 2D finite difference diffusion and reaction models to simulate absorption and reaction in the polymers, and subsequent vapor flux of the chemicals out of the polymers. Experimental vapor flux measurements were used to determine model parameters. Through modeling, an understanding of the surface and subsurface chemistry relationship of simulant to live chemical warfare agent was established.

COLL 93

Ozonation of aromatic hydrocarbon probes at the air-water interface

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The heterogeneous uptake of ozone on liquid and solid atmospheric particles is of major importance for the processing of aromatic hydrocarbons in the atmosphere. Our research explores how aqueous microdroplets carrying aromatic probes react with [O₃(g)] = 40 ppbv–6.0 ppmv during a few microseconds to generate primary ozonide reactive intermediates and a cascade of products. Because the reaction intermediates identified by mass spectrometry would disappear in bulk water >10⁴ times faster than the timescale of the heterogeneous reaction, the observed mechanism is proposed to proceed at the air-water interface. Mechanistic information will reveal the addition of two and three oxygen atoms to the primary products. The fast addition of oxygen atoms to
the parent peak and to first-generation products will be explained based on interfacial processes not observable in bulk water. This study suggests that heterogeneous ozonation reactions have the potential to impact the chemical balance of the atmosphere.

**COLL 94**

**Isotherms for modeling solutions and surfaces**

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Surface properties are crucial to many atmospheric heterogeneous chemical processes including homogeneous nucleation, cloud activation, particle growth at relative humidities below deliquescence, and reactions on particle surfaces. Recently we developed BET-like isotherms of solutions and surfaces that are accurate over the full range of concentration, from infinitely dilute to pure solute. The solution isotherms model solutes as surfaces that sorb solvent. Similar to hydration models, multiple solvent layers are needed to accurately simulate solution behavior. But a key difference between our isotherms and typical hydration models is that the outermost sorbed layer interacts with inner layers and with bulk solvent, which alters the entropy term from that in prior models. In this talk, we will present recent progress including equations for surface concentration of solute and physical interpretation of model parameters.

**COLL 95**

**Single particle computer-controlled Raman (CC-Raman) microspectroscopy analysis as a tool for the characterization and quantification of different types of particles in the atmosphere**

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Physicochemical characterization of individual atmospheric aerosols is essential to improving our understanding of the climate and health effects of atmospheric aerosols, as many important processes in the atmosphere are driven by the size, shape, and composition of individual particles. In contrast, bulk/mass-based methods often lose important information by looking at the ensemble average of particles. In this work we use computer-controlled Raman microspectroscopy (CC-Raman) to obtain information on primary components (such as organic functional groups and carbonate) and secondary components (sulfate, nitrate, and ammonium) of individual particles at
ambient pressure and temperature. We also use for the first time an automated, computer-controlled, method so that a greater number of particles can be analyzed, providing better statistics and the ability to quantify the different populations of particles present. CC-Raman will provide an important tool for studying the complexity and diversity of aerosols, as well as evaluating their climate and health effects.

**COLL 96**

**Black carbon from cookstoves and highway proximity as a risk factor for higher blood pressure in rural China**

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Air pollution in Asia poses large health risks and is a major contributor to climate change. The composition of air pollution from different sources affects its impact on climate and possibly health. We enrolled 280 Chinese women >25-years old cooking with wood stoves, and measured their blood pressure, distance to major traffic routes, and 24-hr personal exposure to PM$_{2.5}$, black carbon (BC), water soluble organic matter (WSOM) and hopanes (motor vehicle emissions) in winter and summer. We used mixed-effects models to estimate associations between air pollutants and blood pressure. Women’s mean 24-hr PM$_{2.5}$ exposure was 88 µg/m$^3$ (range: 9-634); their WSOM exposure was considerably higher than BC (mean: 34 vs. 5 µg/m$^3$). A 1-ln$(\mu g/m^3)$ increase in BC had the strongest association with systolic blood pressure (4.3 mmHg; p<0.001), followed by PM$_{2.5}$ mass and WSOM, with similar effects for diastolic blood pressure. The effect of BC on blood pressure was nearly three times larger...
in women living near the highway (systolic: 6.2 mmHg, 95% CI: 3.6, 8.9 vs. 2.6 mmHg, 95% CI: 0.1, 5.2), though BC exposures were similar. Mean hopane exposure was higher among women in the village closest (~70m) to the highway compared with women in the village farthest (~550m) from the highway (4.6 vs. 1.1 ng/m$^3$; p<0.001). We found that exposure to BC from combustion emissions is more strongly associated with blood pressure than PM$_{2.5}$ or WSOM, and that BC's health effect is larger among women co-exposed to wood smoke and motor vehicles.

**COLL 97**

**Reactions on ambient particles may influence acute and chronic changes in the heart: Effects following exposures of animals with and without hypertension**

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A long-term study of the effects of inhaled air pollution particles on the cardiovascular system was conducted in Riverside California. Animals with high blood pressure or normal blood pressure were exposed to concentrated ultrafine ambient particles (UFP) for 5 hours per day, 4 days per week for 3 months. Blood pressure, heart rate variability and histological changes in the heart were measured. PM samples were collected and analyzed for elemental carbon, trace metals, organic carbon and peroxides (as a measure of oxidant formation on particles). During this long term exposure, there was an unplanned incursion of smoke from wild land fires into the exposure area. Initially during the fires, winds from the northeast (Santa Ana wind conditions) prevented smoke from the fires from reaching the exposure site. However, after about a week the meteorological conditions changed and offshore winds began fumigating the exposure site with ambient particles that were augmented with particles from the smoke. NASA satellite imagery enabled us to pinpoint when the wind direction changed and when the maximum period of exposure occurred. There was a significant acute effect on blood pressure and the data suggest that exposure to smoke from wildfires may alter homeostatic control of cardiac output which might be medically significant. Long term exposures were associated with progressive increases in all exposed animals which were likely to be age-related, however the rate of increase was greater in rats exposed to PM. Chronic exposure to PM also caused histopathological changes in the hearts of all studied strains. The effects ranged from cardiac inflammation caused by 3 months of exposure to UFP in normal and hypertensive rats. Acute changes in blood pressure were correlated with organic constituents of the PM and with peroxides.

**COLL 98**

**Supramolecular control over the gyromagnetic activity of gold nanostars**
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The gyromagnetic activity of gold nanostars (NSTs) with magnetic cores can be controlled by chemical signals, using a supramolecular approach. NSTs were functionalized with methyl viologen dication (MV\textsubscript{2} +), then tethered onto a naphthol (Np)-coated surface using cucurbit[8]uril (CB[8]), a macrocyclic "handcuff" that forms a stable ternary inclusion complex with MV\textsubscript{2} + and Np in water. Increasing the CB[8] concentration causes the NSTs to become fully immobilized, but treating the bound NSTs with neurotransmitters such as dopamine restores their ability to generate gyromagnetic signals. This chemionic system provides a unique example of synthetic neurotransmission, with potential applications in the design of chemically triggered nano-mechanical devices.

COLL 99

Porous (nano)materials: Properties, self-assembly, and applications

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Porous materials are of particular interest because of their multifunctionalization that can involve the surface, the channels and the channel entrances. The talk will illustrate some of the recent results on microporous and mesoporous silica based nanoparticles. In particular examples using the crystalline allumino silicates, zeolite L, and mesoporous organosilicates will be discussed since these materials can act as nanocontainers and due to their biocompatibility used for biomedical applications. The different functionalization of their surface will be discussed, in particular with the aim to show that the particles can be decorated with different functional groups including biocompatible molecules and are able to perform drug and DNA or RNA delivery inside the cell \cite{1}. The delivery can be probed by a kinetic analyses after the nanoparticles internalization. In particular using confocal fluorescent microscopy it is possible to follow the release of each single component as well as the positioning of the nanocontainers in real time and space. Such achievement allows us to study the fate of the different units and their release time. Also it will be shown how the molecules entrapped in the ordered channels can become active components. The alignment of electroactive molecules inside the narrow channels of a zeolite L, resulted in the formation of molecular wires. The molecular wire length is tunable between 30 and 100 nm and electrical measurements on the 1D assemblies were performed. Finally an ultra-high (> 2000\%) room-temperature magnetoresistance was observed applying only a few mT \cite{2}.

Finally it will be discussed how the morphology of such nanocontainers can be important for the creation of patterned substrates on which different cells can preferentially adhere \cite{3}. The growth and proliferation of the cells can be selectively
controlled only on small areas of the surfaces as well as promoted in a soft matrix
sandwiched in between the rigid scaffolds [4].


2012, 51, 3716-3720.


COLL 100

Ikebana chemistry as a route to multifunctional gold nanoparticles with
biomimetic properties

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The use of gold nanoparticles as scaffolds for the sequential attachment of thiolate
ligands with diverse functionalities, here referred to as ikebana chemistry, represents a
facile and attractive route to multifunctional supramolecular materials. As an increasing
variety of chemical and supramolecular functionalities are being made commercially
available as thiolated reagents, this assembly strategy is becoming more and more
realistic and powerful. Here we demonstrate the design and assembly of monolayer
protected clusters (MPCs) of gold, with a range of complex biomimetic properties such
as spontaneous membrane insertion and charge transfer across membranes under
non-equilibrium conditions. These properties are conferred to the clusters by the choice
of functionalities that are integrated in the ligand shell. These include both functional
and structural moieties such as crown ethers, polyethylene oxide chains, carboranes
and redox-active domains. The results reported here are preliminary and part of
ongoing research.

COLL 101

Thiolated metal clusters as new class of photosensitizers in light energy
conversion

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Glutathione capped metal nanoclusters (Aux-GSH NCs) exhibit molecular like properties
and their excited state properties can be controlled through numbers of metal atoms
and capping ligands. Their long lived excited state (lifetime $\sim 800$ ns) and reversible reduction ($E^0 = -0.63$ V vs. RHE) and oxidation ($E^0 = 1.51$ V vs. RHE) potentials make them suitable as visible sensitizers for driving the water splitting reaction. When a mesoscopic TiO$_2$ film sensitized by Au$_x$-GSH NCs was used as the photoanode in a photoelectrochemical cell we can generate photocurrent under visible light irradiation with a photoconversion efficiency of 2%. Additionally, sensitizing Pt/TiO$_2$ nanoparticles with Au$_x$-GSH NCs has been explored in an aqueous slurry system and irradiating with visible light resulted in hydrogen production. These metal nanoclusters which serve as a new class of visible photosensitizers offer new opportunities as light harvesting assemblies.

**COLL 102**

**Iron oxide nanoparticles for magnetic mediated hyperthermia, controlled drug delivery and ovarian cancer tumor targeting**

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In the last decades, the progress done in the preparation of magnetic nanoparticles has renewed the interest of applying magnetic induced hyperthermia when using nanoscale probes. At the same time, the local heat effects observed at the nanoparticle surface have pushed towards the use of magnetic nanoparticles as drug delivery tolls with heat triggered release mechanism.

A wide variety of iron-based nanocrystals produced by thermal decomposition method, a non-hydrolytic approach, have been reported and they were here studied for what concerns their heat efficiency under alternating magnetic field (AMF) exposure. We found that, iron oxide nanocubes of 19-35 nm edge, cobalt ferrite nanocrystals at different shapes and cobalt fractions and iron oxide-gold dimers, made of a gold sphere sharing a small interface with iron oxide nanoparticles, are all efficient materials in terms of specific adsorption rate values under AMF of field amplitudes and frequencies that are biological safe for patients. Many efforts were also devoted by us to coat those nanoparticles with thermo-responsive linkers or thermo-responsive polymer shell and then attaching/encapsulating doxorubicin as drug agents for achieving heat-mediated chemotherapy.

Finally, in a comprehensive study we have designed and functionalized iron oxide nanoarticles with specific antibody fragments (AFRA) to target ovarian cancer cells. The *in vitro* and *in vivo* studies carried out in collaboration with some of the partners of the FP7 Magnifyco project, have allowed to elucidate the effect of the targeting in relation to the nanoparticle size. Remarkable, the *in vivo* ovarian cancer tumor targeting has been also demonstrated with 20 nm particles. An overview of these results will be presented. Besides the partial success achieved in some of those studies, much can be learned from our experience.
Using photoresponsive nanoparticles and molecular switches to control chemistry

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In this presentation several examples of how nanoparticles decorated with photoresponsive molecules can be used to control chemical reactions will be discussed. The general theme of the presentation is 'molecular switching', which is a field that aims to use small molecules to turn 'on' and 'off' processes relevant to chemical and biochemical processes. Despite the fact that numerous examples of successful molecular photoswitches (those that reversibly change their shape and properties in response to light) have been reported, there still exist several issues limiting their use in biological applications. Many of these limitations can be potentially overcome by decorating the molecular switches onto photoresponsive nanoparticles. The examples presented will include 1) how nanoparticles lanthanide-doped upconverting nanoparticles can harness near infrared light and convert it into the ultraviolet and visible light required to trigger the photoreactions of organic compounds, 2) how polymer-encapsulated nanoparticles can provide the local hydrophobic environment to allow effective photoreactions, and 3) how gold nanoparticles can be used to generate the heat needed to break down anchored organic compounds and release singlet oxygen.

Nanoparticle-stabilized nanocapsules for direct delivery of proteins and siRNA to the cytosol

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We have employed gold nanoparticles (AuNPs) as building blocks for self-assembled delivery vehicles. These studies have used AuNPs to stabilize oil-in-water emulsions, providing nanoparticle-stabilized capsules (NPSCs) (Figure 1). Through appropriate choice if particle functionality and oil we have been able to generate ~100 nm capsules. These capsules are stable in serum, with in vitro cell studies indicating effective delivery of hydrophobic drugs. More recently, these capsule have been used to deliver both proteins and siRNA directly to the cytosol, avoiding the myriad challenges faced with endocytotic strategies.
Chemical processes on oxide surfaces: New insights gained by IRRAS-studies on well-defined single crystal surfaces

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One of the most powerful techniques to address fundamental questions about the nature of chemical species bound to surfaces is vibrational spectroscopy. In case of metals, results from related techniques (EELS, IR) have contributed substantially to the rather concise picture on metal surface chemistry which is available today. In particular IRRAS (infrared reflection-absorption spectroscopy) has provided characteristic fingerprints allowing to identify metal-bound adsorbate species formed upon reaction with the substrate or with coadsorbed species.

In case of oxides, unfortunately, the application of IRRAS has been severely hampered by technical problems arising from the low reflectivity of oxides in the IR-regime. Although a large set of IR data is available for powders, prior to 2008 there was only a single paper with IRRAS data for an well-defined model systems oxide, rutile TiO$_2$(110) [1].

By employing a state-of-the-art infrared (IR) spectrometer modified to fit an ultrahigh vacuum (UHV) chamber [2], we were able to overcome these technical problems, In addition to titania substrates (both, rutile and anatase) we were also able to record high-
quality IR-spectra for other oxides, including ZnO and ceria. In the latter two cases there are no previous IRRAS studies published in the literature.

In this presentation we will discuss the results obtained in these previous studies and demonstrate how high-quality IR-spectra recorded for single crystal surfaces greatly simplify the interpretation of IR data measured for powders. In addition, the availability of reference data for CO adsorbed on well-defined oxide substrates allows for using CO as a probe molecule to determine defect densities on powder samples. This will be demonstrated for the cases of titania powder particles [3].


COLL 106

Glycols as models for biomass: Surface chemistry and mechanism of hydrogen formation on rutile TiO₂(110)

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Biomass conversion to biofuels and value-added chemicals has been receiving increased attention in recent years. Due to the large number of functional groups in biomass, its utilization is rather complex and therefore hard to understand and optimize. In this work, we use several simple glycols, such as ethylene glycol and 1,2- and 1,3-propylene glycols, as biomass surrogates, and probe their conversion on a model reducible oxide surface, rutile TiO₂(110). For ethylene and 1,2-propylene glycols, two reaction channels are observed: one leading to alkenes, the other to aldehydes/ketones. The alkene formation dominates at low glycol coverages, while the aldehydes and ketones are primarily observed at high coverages. For 1,3-propylene glycol, an additional C-C cleavage channel yielding formaldehyde and ethylene, and a disproportionation channel yielding 1-propanol and acrolein are observed. At high coverages, the carbon containing products are accompanied by hydrogen. This is in sharp contrast to alcohols, from which only water is observed. Experiments with OD-labelled glycols show that hydrogen originates exclusively from the glycol hydroxyl groups. Increasing the steric hindrance around the OD groups by methyl side groups is found to inhibit and eventually eliminate hydrogen formation. Damaging the surface order or scavenging the available surface charge of TiO₂(110) are also shown to completely suppress hydrogen formation. Combined, these results suggest that hydrogen formation results from proximal glycol pairs, and that the redox reaction is driven by defect electrons of TiO₂(110).
Role of excess charge carriers on the surface chemistry of reducible metal oxides

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An overview will be given of ongoing theoretical studies of reactivity on prototypical reducible oxide surface rutile TiO$_2$(110), and CeO$_2$(111).[1-7] The excess charge in these systems consists of localized polarons, centered on metal d and f states for Ti and Ce sites respectively, which can move dynamically through the oxide lattice and take part in the redox chemistry of adsorbed surface species such as CO, O$_2$, CO$_2$, and small organic molecules. The role of bulk and surface defects in creating excess electrons, which form polarons, and their dynamics, will be discussed. Emphasis will be placed on the ability polarons to perform surface redox chemistry and illustrated with examples from our own work. One issue, which will be discussed, is the potential for non-adiabatic surface to adsorbate charge transfer and its impact on rates on otherwise thermodynamically favorable reactions. In a final segment, the CO oxidation reaction will be used as a model probe reaction to allow us to compare the same reactivity, on the same surfaces, with and without supported metal nanoparticles.


Structure comparison of rutile TiO$_2$(110) and anatase TiO$_2$(101) and their interfaces with water

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Much attention has been focused on the surface science of titanium dioxide due to its numerous scientific and industrial to its applications in photocatalysis, electrochemistry, active coatings, gas sensors. Among these studies, many have focused on the interaction of water with rutile and anatase (110) surfaces, 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 environments (<1x10⁻¹⁰ mbar). Here we present work that has characterised the atomic scale structure and composition of the liquid water interface using surface X-ray diffraction. For rutile (110), a 2x1 an ordered interface of terminal hydroxyls is formed, with water in the second layer. The clean anatase (101) in UHV is found close to that calculated, with a mixture of hydroxyls and water at the interface with an ultrathin layer of H₂O.

COLL 109

Tuning the activity and stability of copper based catalysts with reducible oxides

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The natural abundance of copper and cuprous oxide (Cu₂O), its tunable electronic properties and its optimal catalytic performance for reactions from CO oxidation, water-gas shift (WGS) to methanol synthesis have made it a prime target for catalytic research. While the controlled synthesis of nanoscale cuprous oxide particles is being actively pursued to optimize its properties, the Achilles heel of Cu₂O catalysts has been its deactivation by complete oxidation to CuO or reduction to Cu, in both cases losing the critically active catalytic Cu⁺ centers. The oxidation of CO (CO+1/2O₂=CO₂) is the archetypal heterogeneous catalytic reaction, playing a central role in the advancement of fundamental studies, the control of automobile emissions and industrial oxidation reactions. Copper-based catalysts were the first reported to run CO oxidation at room temperature, but their lack of stability at the elevated reaction temperatures used on automobile catalytic converters, in particular the loss of the most reactive Cu⁺ cations, leads to their deactivation. Using a combined experimental and theoretical approach, we show how the incorporation of Ti cations in a Cu₂O film leads to the formation of a stable mixed-metal oxide, with a Cu⁺ terminated surface highly active for CO oxidation.[1] The oxidation of CO during the WGS reaction (CO+H₂O=CO₂+H₂) occurs in this case under an overall reducing environment. We show how the formation of a multifunctional metal-oxide interface with ceria nanoparticles allows the stabilization of
critical intermediates for an efficient associative reaction mechanism.[2] We will finally show that a similar metal-oxide interface can help to activate copper for the thermal reduction of CO₂.

[1] “Importance of the Metal-Oxide Interface in Catalysis: In-situ Studies by Ambient-Pressure XPS of the Water-Gas Shift Reaction” K Mudiyanselage, SD Senanayake, L Feria, S Kundu, AE Barber, J Graciani, AB Vidal, S Agnoli, J Evans, R Chang, S Axnanda, Z Liu, JF Sanz, P Liu, JA Rodriguez, DJ Stacchiola


**COLL 110**

**Chemical accuracy for molecule-surface interactions: Ab initio energies and entropies**

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A hybrid method that combines MP2 on cluster models with DFT+dispersion on periodic models (plus DCCSD(T) corrections) is presented that yields binding energies of molecules on (simple) metal oxide surfaces *ab initio* and with chemical accuracy. Examples are the binding of CO and CH₄ on Mg(001), of H₂, CH₄, CO and CO₂ on the internal surfaces of metal organic frameworks (MOF), as well as the adsorption of hydrocarbons in zeolites. Entropies of adsorption can also be calculated with chemical accuracy from vibrational partition functions calculated by DFT+dispersion, when anharmonicities are included. This is shown for adsorption of CH₄ on MgO(001) and in a zeolite with Bronsted sites (H-chabazite).

**COLL 111**

**In situ sum-frequency vibrational spectroscopy of electrochemical interfaces with surface plasmon resonance**

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Electrochemical (EC) reactions are crucial in many applications, yet most EC analytical tools lack the sensitivity to access molecular-level information of reactants and products. By combining sum-frequency vibrational spectroscopy (SFVS) and surface plasmon resonance (SPR) at EC interfaces, we demonstrated the feasibility of measuring in situ and real-time vibrational spectra during EC reactions at noble metal electrodes. Application of the technique to EC reactions at a gold surface helped understand how the surface in a basic solution was oxidized and reduced during a cyclic voltammetry cycle. Study of desorption of a thiol self-assembled monolayer from gold through EC reactions in a basic solution showed that contrary to intuition, the desorbed thiols by reductive reaction remained as an ordered layer near the gold interface, but did diffuse away if they are desorbed oxidatively from gold.¹


Freezing and melting of salt hydrates next to solid surfaces probed by infrared-visible sum frequency generation spectroscopy

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Understanding the freezing of salt solution near solid surfaces is important in many scientific fields. Here, we have used sum frequency generation (SFG) spectroscopy to
study the freezing of salt solutions next to a sapphire substrate. For NaCl solutions, during cooling we observe two transitions; the first transition corresponds to segregation of concentrated brine next to the sapphire surface as we cool the system down into the phase region where there is a coexistence of ice and brine. At this transition, the intensity of the ice-like peak decreases, suggesting the disruption of hydrogen bonding by sodium ions. The second transition corresponds to the formation of NaCl hydrates with abrupt changes in both SFG intensity and the sharpness of spectral peaks. The similarity in the position of the SFG peaks with those observed using IR and Raman spectroscopy indicates the formation of NaCl.2H₂O crystals next to the sapphire substrate. In my talk I will also discuss our recent results on freezing and melting of MgCl₂ and CaCl₂ hydrates.

COLL 113

Sum frequency generation microscopy of surfaces

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Sum frequency generation spectroscopy (SFG) is a useful technique to study molecular properties of surfaces. As a second-order technique it is uniquely sensitive to the average organization of molecules at the surface. However, as most surfaces are spatially heterogeneous, it is difficult to interpret the spectrum as single domain. The development of SFG into a microscopy has allowed a more detailed and accurate analysis of the spatio-spectro-temporal evolution of the surface chemistry. The SFG microscope development will be presented, as well as the use of compressive sensing and the application toward corrosion inhibition and self-assembled monolayers.

COLL 114

Development of compressive sensing-sum frequency generation microscope

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A new surface microscope, compressive sensing sum frequency generation microscope (CS-SFG), is developed to study the Langmuir–Blodgett monolayer on solid and liquid substrate together with Brewster Angle Microscope (BAM). Compared to the traditional sum-frequency generation microscope, the new method, compressive sensing (CS), enables the use of a “single pixel detector” such as a photomultiplier tube (PMT) or a photodiode instead of the CCD or CMOS chips to obtain images in a unique and efficient manner. More than the traditional advantages of SFG microscope, which has highly surface specific and allows the operation in ambient conditions for various interfaces with both vibrational spectroscopy and the orientation of the functional groups information, the new CS-SFG can reconstruct the imaging by smaller number of measurement and highly increase the resolution by signal dilution. Furthermore, as
single pixel detector, such as PMT, can be used in CS-SFG to capture the weak nonlinear SF signal and chemically image, it possible to get the image with high efficiency and less image distortion from dark noise and read-out noise, and therefore, with better quality. Brewster Angle Microscope has good surface selectivity and flexibility in different system. Different from SFG, which resolution comes from Fresnel coefficient, BAM provides more information about the refraction index difference. Using BAM together with CS-SFG could get the chemical imaging on the surface more comprehensively, and better analyzing the properties of surface molecules and chemical process.

**COLL 115**

**Unified photoemission spectroscopic picture of defect-driven charge carrier physics at an organic semiconductor/metal oxide interface**

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Interfaces between metal oxides and organic semiconductor molecules are crucial to the efficient operation of next-generation optoelectronic devices, including organic photovoltaics, field effect transistors, and light-emitting diodes. The electronic interactions at such interfaces are complex and not well understood, preventing rational design of such devices from fundamental principles. Significantly, the electronic properties of metal oxide surfaces can vary enormously with different preparation methods, yielding fundamentally different band alignment and carrier dynamics.

To address this problem, we have undertaken a unified spectroscopic study of the prototypical interface between ZnO and C₆₀⁻. By combining classic interface spectroscopies of ultraviolet photoemission (UPS) and inverse photoemission (IPES) with the cutting-edge abilities of two-photon photoemission (TPPE) and resonant photoemission spectroscopy (RPES), we provide unprecedented insight into the charge carrier physics at the hybrid organic/metal oxide interface. With UPS and IPES, we probe the interfacial energy level alignment. Using TPPE for the first time on a complex interface such as that of thin film ZnO and C₆₀, we spectroscopically monitor defects within the ZnO bandgap. Finally, we also report the first application of the RPES core-hole clock method to charge carrier physics in a metal oxide near an organic semiconductor interface.
We apply this unified spectroscopic survey to highly conductive thin-film ZnO samples with differing surface treatments, studying their effect on the interfacial electronic structure. We demonstrate that small but significant shifts in the properties of the ZnO film result in dramatic changes in the interfacial electronic interactions with C₆₀. Drawing on the full range of photoelectron spectroscopies, we derive an atomistic picture of the electronic interactions at the hybrid organic/metal oxide interface. This model provides detailed insight into the carrier physics near ZnO interfaces, and also yields an understanding of the fundamental physical principles of semiconductor interfaces, expected to be broadly applicable.

COLL 116

Localizing newly introduced ligands on the surface of CdS nanocrystals

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The manipulation of ligands on nanocrystal (NC) surfaces is crucial in solution processing these materials into optoelectronic devices and fluorescent labels for biological imaging. With a fluorescence resonance energy transfer (FRET) based approach, we study the relative dispersion of freshly introduced ligands on the surface of NCs. In our system, a green and a red dye functionalized with NC binding groups were chosen as donor and acceptor respectively. FRET between these ligands indicate they are bound on CdS NC within the Förster distance of 25 Å, despite the fact that only an average of three new ligands are covalently attached to the NC surface. This may be an indication of cooperative binding, where the first binding event modifies the structure on the surface of the NC, thus leading to a change in binding constant for the second ligand. Cooperative binding is usually observed in biological systems, and haven't been reported in NC for organic ligands, especially at the low concentrations in our experiment.

COLL 117

In-situ X-ray absorption spectroscopy study of metal/water interfaces

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Most of the electrochemistry processes occur within the electrical double layer (EDL) at the electrode/electrolyte interfaces. In spite of some classic EDL theories, very limited experimental information is available about these solvent or solute species within such EDLs. We have developed in-situ liquid cells to study such electrolyte/electrode interfaces by means of soft x-ray absorption spectroscopy (XAS), particularly in total electron yield (TEY) mode. Because those secondary electrons can only penetrate extremely short distance in condensed matters (typically several nm in water), the information we can obtain from XAS TEY spectra are surface/interface sensitive. With such in-situ XAS technique, we characterized the interfacial water at different metal electrode surfaces, including Au, Pt and Ni. It was found that the interfacial water layer has significantly different hydrogen-bonding network structure compared to the bulk water. Under different bias, the polar water molecules will respond to the external electrical field and reorient at the gold electrode surface, which significantly alters the amount of distorted or broken hydrogen bonds.[1]


COLL 118

In situ XPS and NEXAFS investigation of the thermally-induced structural evolution of advanced amorphous carbon-based surfaces

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Silicon oxide-doped diamond-like carbon (SiOₓ-DLC) coatings are fully amorphous thin-film materials consisting of two interpenetrating networks, one being a hydrogenated amorphous carbon (a-C:H) network and the other a silica glass (SiOₓ) network. At temperatures above 150°C, pure a-C:H films undergo a rapid degradation that starts with the evolution of hydrogen and is followed by the conversion of sp³ bonds to sp². However, SiOₓ-DLC exhibits much lower susceptibility to oxidative degradation, and much higher thermal stability compared to a-C:H. This makes SiOₓ-DLC an attractive material for many applications, including for the development of next generation hard disk drives which require novel overcoat materials that are thermally stable up to temperatures above 500°C. Even though it is well-established that SiOₓ-DLC possesses superior thermal stability and oxidation resistance relative to a-C:H, the scientific basis for this behavior is not understood. To investigate this, a combined in situ XPS and NEXAFS study was performed. Changes in the surface chemistry and bonding configuration of SiOₓ-DLC (e.g., silicon oxidation state, carbon hybridization state) could be accessed in situ at temperatures up to 450°C. A novel methodology for processing NEXAFS spectra, which makes it possible to account for the presence of a carbonaceous contamination layer on an air-exposed material, was developed. This allowed quantitative evaluation of the carbon hybridization state in the film as a function
of the annealing temperature. These experimental results could be well fit with a thermal activation-based model that describes the structural transformations occurring in vacuum in SiOₓ-DLC as a function of time and temperature. To determine the environmental dependence of the surface structural evolution of SiOₓ-DLC, the results of the in situ XPS/NEXAFS investigation were compared to those for SiOₓ-DLC samples heated in air, showing a strong effect of atmospheric oxygen.

**COLL 119**

**Probing Ni-graphene interface using Raman spectroscopy**

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Theoretical simulations have shown that due to the hybridization of Ni d-electrons with the π-orbitals of graphene, graphene phonon dispersion is significantly altered and there is no Raman signal from graphene on Ni(111) due to the suppression of the Kohn anomaly (Nano Lett, 2010, 10, 4335-4340). In this work, we deposit Ni thin film by thermal evaporation onto mechanically exfoliated graphene, few-layer graphene (FLG), and graphite, and probe the Ni-graphene interface using Raman spectroscopy. When the sample is annealed in forming gas, Ni(111) thin film is produced on graphene, FLG, and graphite. We observe the disappearance of Raman signals from graphene underneath Ni(111) and provide direct experimental evidence for the suppression of the Kohn anomaly in this system.

**COLL 120**

**Direct measurement of chemical distributions in heterogeneous coatings contaminated with chemical warfare agents and associated simulants**

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Characterization of the absorption of highly toxic chemicals into permeable materials is paramount for hazard assessments due to these types of contaminated materials as well as designs for decontamination approaches. Of particular interest is the interaction of chemical warfare agents (CWA) and their simulants with multi-layer, polymeric coatings that are used on military assets. For this study, MIL-specification polyurethane and alkyd based paint coatings were applied to aluminum and silicon substrates and contaminated with bis(2-chloroethyl) sulfide (distilled mustard, blister agent HD) and O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX), an organophosphate nerve agent, as well as their respective simulants, 2-chloroethyl ethyl sulfide (CEES) and dimethyl methylphosphonate (DMMP), via liquid phase deposition. Measurements of the materials cross-section were then performed by scanning electron microscopy
(SEM) coupled with energy dispersive spectroscopy (EDS) in order to directly determine chemical species distribution in subsurface layers. SEM-EDS probing of the surfaces and cross-sectional interfaces of the contaminated coatings provided spectral and elemental mapping data specific to each contaminant-material system. The results demonstrate SEM-EDS capability to detect and spatially-resolve unique elemental signatures of CWA and simulants within military coatings. The visual and quantitative results reveal substrate subsurface contaminant distributions, provide estimations for molecular diffusion coefficients as a function of contaminant and substrate, and expose material characteristics and components that affect contaminant transport into coating materials. Comparisons are made between live agent and simulant as well with regards to subsurface absorption behavior.

COLL 121

King-Wells meets Eley-Rideal in outer space: The detection of a new source of CO$_2$ in the universe

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We have discovered a new source of CO$_2$(ice) in outer space using classical methods of surface science. When water ice is exposed to Lyman-$\alpha$ (10.2 eV) radiation, OH radicals are produced. Carbon monoxide gas, incident on the surface of the ice, reacts efficiently with the surface hydroxyl radicals likely producing HOCO which then decomposes to CO$_2$(ice) at 76 K. Kinetic measurements of the King-Wells type indicate that the cross section for the reaction is $\sim 6 \times 10^{-20}$ m$^2$ and that the reaction occurs by a direct Eley-Rideal process without the involvement of a mobile precursor CO species. These findings may explain the mystery of the high relative abundance of CO$_2$ (ice) compared to CO$_2$ (g) in space.

COLL 122

Adventures in catalytic nanospace: The selective oxidation of methanol

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Methanol is oxidised in a selective manner to formaldehyde via the methoxy surface intermediate, but is combusted via the non-selective surface intermediate, the formate. I will report on the stability, formation, structure and active sites for this reaction on Cu(110), determined using a molecular beam reactor, TPD and STM. Only very particular sites are able to selectively oxidise methanol, and these are the three-fold coordinate oxygen sites, while the majority are four-coordinate.
Copper is actually a relatively poor catalyst for methanol oxidation, and oxides have become commercialised for the reaction. The basics learned from surface science apply also to the reaction on the best of these oxides, iron molybdate \((\text{Fe}_2\text{(MoO}_4)_3\)) with methoxy and formate intermediates shown to be involved. I will describe our understanding of this reaction on the high area catalyst oxide surfaces, and the beginnings of work using surface science methods and oxide single crystals, trying to fabricate iron molybdate surfaces and to investigate their reactivity.

**COLL 123**

**Rational catalyst design using DFT calculations**

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Catalysts are commonly developed by experimental trial-and-error approaches. It is one of the ultimate goals in chemistry to design rationally catalysts theoretically. In this talk, I will use two examples to illustrate that DFT calculations are very powerful to understand catalytic processes at atomic level and it is possible to rationally design catalysts in heterogeneous catalysis.

**COLL 124**

**David King's legacy of adsorption calorimetry on well-defined surfaces: Where it has taken us**
David King and his group developed the first calorimeter that could measure heats of adsorption on the well-defined surfaces of single crystals with sufficient precision to reveal new understanding of surface chemistry. Since then, other groups including our own have adopted this technique and made substantial extensions, including: (1) detector improvements that allow routine measurements from 100 to 350 K with high precision (a standard deviation of 1.3 kJ/mol with gas pulses that contain only 1% of a monolayer), (2) metal adsorption and adhesion energies during thin film growth, (3) energetics of metal nanoparticles versus size, (4) measurements of electrochemical adsorption and reactions at liquid/solid interfaces, (5) measurements of protein adsorption, and (6) transient measurements of heat signal lineshapes during two-step reaction mechanisms (e.g., molecular adsorption followed by dissociation) that give the heats for both steps and the rate constant for the second step during every gas pulse. These extensions and their applications will be reviewed to assess the current state of adsorption calorimetry on well-defined surfaces, and its future prospects.

Work supported by NSF grant #CHE-1010287.

COLL 125

Understanding fuel cell and heterogeneous catalytic reactions from an electrochemical surface science perspective

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The need to move away from purely fossil fuel based transport modalities (due to resource limitations, legislative imperatives and environmental issues) is re-focussing research efforts towards the development of new approaches based on biofuels and electric/hybrid vehicles including Battery Electric Vehicles and Fuel Cell Electric Vehicles (FCEVs). Although each of these avenues offers a partial solution towards an overall energy efficient transport strategy, each has its drawbacks therefore inhibiting any one approach from commanding overall commercial acceptance. Fuel cell technology for example has the potential to find use in many applications of varying scale, from small mobile devices to large transport vehicles but suffers from a number of technical limitations such as membrane, catalyst and support stability, poor electrocatalytic activity (even for the best electrocatalysts) and fuel crossover. Similarly, more active and selective heterogeneous catalysts are required in order to reduce waste, save energy and clean up the environment. In both of these areas highlighted, fundamental understanding of the solid-liquid and solid-gas interface together with in situ characterisation of surface reaction mechanism using operando spectroscopic methods is essential in order to facilitate the design of new and superior catalytic materials. Examples of how surface science and electrochemical surface science methods may be used to address these challenges will be discussed with particular
emphasis on bimetallic surfaces, ionomer-metal interfaces, oxygen reduction and enantioselective hydrogenation reactions.

**COLL 126**

**Recent progress for density functional theory calculations towards reactions at solid-liquid interface**

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The last twenty years have witnessed the wide application of density functional theory calculations in surface science and catalysis starting from King's group at Cambridge in early 1990s. Many fundamental properties of surfaces including the kinetics of catalytic reactions can now be routinely calculated within days or hours on modern computers, which have not only speeded up the research progress but also reshaped the research methodology in the field. Theoreticians are now at a stage to look into some even more complex phenomena, such as those related to electro-photocatalysis at the solid-liquid interface. In this talk, I will introduce the new methodology development at Fudan to simulate the solid-liquid interface reactions and the solid-solid phase transition. Examples will be given to show how theory can help to solve the hydrogen evolution chemistry in fuel cell and the anatase-to-rutile transformation in photocatalysis.

2. Li, Y.-F.; Liu, Z.-P. "Particle Size, Shape and Activity for Photocatalysis on Titania Anatase Nanoparticles in Aqueous Surroundings" J. Am. Chem. Soc. 2011, 133, 15743

**COLL 127**

**Influence of immobilized enzyme on photoluminescence properties of mesoporous silicon surface**

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Acetylcholinesterase immobilized p-type porous silicon surface was prepared by covalent attachment. The immobilization procedure was based on support surface chemical oxidation, silanization, surface activation with cyanuric chloride and finally covalent attachment of free enzyme on the cyanuric chloride activated porous silicon surface. Different pore diameter of porous silicon samples were prepared by electrochemical etching in HF based electrolyte solution and appropriate sample was selected suitable for enzyme immobilization with maximum trapping ability. Porous silicon showed strong photoluminescence with maximum emission at 643 nm and immobilization of acetylcholinesterase on porous silicon surface cause considerable increment on the photoluminescence of porous silicon material while acetylcholinesterase free counterpart did not exhibit any fluorescence in the range of 635-670 nm. The activity of the free and immobilized enzymes was evaluated by spectrophotometric method, and surface modification was studied through field emission scanning electron microscopy, EDS, FT-IR analysis, and photoluminescence measurement by utilizing the fluctuation in the photoluminescence of virgin and enzyme immobilized porous silicon surface. The immobilized enzyme was observed to retain hydrolysis response upon incubation with acetylthiocholine iodide with enhanced stability, easy separation from the reaction media and significant saving of enzyme. It was believed that immobilized enzyme can be exploited in organic and biomolecule synthesis possessing technical and economical prestige over free enzyme.

COLL 128

Effective route for the room temperature formation of platinum nanomaterials in aqueous solutions

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We present a facile one-pot synthetic route for the production of platinum nanomaterials via a simple proton beam irradiation process at room temperature. Hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were used as stabilizing reagents for the preparation of Pt nanomaterials. Size-and shape-controlled platinum nanostructures were prepared by simply varying the amount of added isopropyl alcohol to the reaction mixture. The morphology of Pt nanoparticles was controlled by the proton beam current and the duration of irradiation. The characterization was done by using UV-Vis absorption spectroscopy, TEM, and EDS analyses.

COLL 129

Earth abundant FeS₂ nanomaterials for photovoltaic and catalytic applications

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Iron pyrite FeS$_2$ are abundant and nontoxic materials in nature. Recently, we have attracted attention for developing low-cost fabrications of catalytic electrode and photovoltaic devices using solution processes. The size of pyrite FeS$_2$ NCs were around 15 with well-controlled. In the photovoltaic applications, we have demonstrated a polymer solar cell based on poly(3-hexylthiophene) (P3HT)/FeS$_2$NCs hybrid and a heterojunction photodiode consisting of a device structure of ITO/ZnO/FeS$_2$NC/MoO$_3$/Au. The both devices exhibited an excellent photoresponse with a spectral response from visible to NIR wavelengths. Besides, we also demonstrated other promising photovoltaic applications using FeS$_2$NCs pyrite ink to fabricate a cost-effective counter electrode (CE) in dye-sensitized solar cells (DSSCs). FeS$_2$ NC has exhibited excellent electrochemical catalytic activity and remarkable stability in replacing expensive Pt catalysts as a low-cost CE material in DSSCs. Devices using FeS$_2$ NC-based CE show promising power conversion efficiencies comparable to those using the Pt CE. Overall results indicate that earth-abundant FeS$_2$ NC is an interesting candidate of light absorbent and catalysts, which can substantially lower the cost of photovoltaic and DSSCs in future commercial applications.

**COLL 130**

**Gelation ability of lecithin organogelators against various oils**

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Lecithin organogels consisting of reverse worm-like micelles typically form by combination of lecithin and water in a nonpolar organic solvent. The advantages of lecithin organogels include their biodegradability, biocompatibility, and long-term stability. In addition, these organogels are easy to prepare and can solubilize molecules of different polarities. These advantages may enable the application of lecithin organogels to a variety of commercial products such as cosmetics, medicines, and foods. In this system, water is an important constituent for the formation of reverse worm-like micelles. Previous reports have indicated that urea, sucrose fatty acid esters, D-ribose, polyglycerols, ascorbic acid, and multivalent carboxylic acids can replace water as the important constituent. In this work, the gelation ability of lecithin organogelators against various oils such as hydrocarbons, fatty acid esters, fatty acid triglycerides, and silicones was investigated as a fundamental study for application development.
Preparation and characterization of electrospun EDTA/PVDF blend nonwoven mats

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The representative SEM images of the PVDFNM that were obtained using different solvent systems (Fig. 1a-b: 20 wt % PVDF dissolved in DMF, Fig. 1c-d: 20 wt % PVDF dissolved in DMF/Ace cosolvent) is shown in Fig.1

Clearly, fibrous morphologies (diameter = 476±145nm) were generated from the PVDF stock solution that was prepared with the DMF/Ace cosolvent and the bead-on-string structure was observed when the solvent system was changed from DMF/Ace cosolvent to pure DMF(diameter = 234±65nm). Although the PVDFNM that was produced from the DMF-based PVDF stock solution comprised thinner fibers than that produced from the DMF/Ace-based PVDF stock solution, the DMF/Ace cosolvent system was used in the subsequent experiments because of its reproducibility and stability in production of PVDFNM. The SEM images of the EDTA/PVDFNM that was prepared by separately adding 0.06 g (Fig. 2a)and 0.3 g EDTA (Fig. 2b) in 1 mL of PVDF solution are displayed in Fig.2
Notably, the surface of the electrospun PVDF fiber was decorated with EDTA particles and the density of the EDTA decoration increased with the EDTA loading in the PVDF stock solution. This study is intended to provide a novel extraction material and procedure for the removal of soluble, sparingly soluble and insoluble heavy metal ions or particles from chemical sewage, such as that which drains away from electroplating or electropolishing plants.

COLL 132

Studies of fluorescence behavior of lipid-fluorescent dyes in liposomes

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Liposomes (lipid vesicles) have been widely used as nanoparticle systems for drug delivery, diagnostics, imaging and for basic research as model membranes. Incorporation of non-exchangeable lipid-fluorescent dyes into liposomes have allowed researchers to trace the distribution in biological systems and binding/uptake of liposomes into cells. A large number of lipid conjugated fluorescent dyes have been used for the generation of fluorescent liposomes, however fluorescent liposomes used by most researchers are not optimized for the amount of dyes to minimize self-quenching and for optimal fluorescent intensity. In this study the fluorescence behaviors for a number of DHPE-conjugated fluorescent dyes in different types of liposomes are
investigated. The fluorescent intensity are monitored as a function of dye/lipid ratio for liposomes composed of fluid membranes as well as solid membranes. The results indicate a distinct difference in the fluorescence behavior for each dye in liposomes with different fluidity. The results is very valuable and will serve as a guideline for researchers to design their fluorescent liposome systems.

COLL 133

Electronic "hole" induced ultrahigh activity of CeO$_2$ supported monomeric VO$_x$ for selective oxidative dehydrogenation of benzyl alcohol

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Selective oxidative dehydrogenation (ODH) of, in particular, alcohols to aldehydes, is the process with paramount importance in chemical industries. Recently, vanadium oxide species supported at ceria have been shown to give some amazing features in such reactions. In the current work, we performed total energy density functional theory (DFT) calculations corrected by on-site Coulomb interaction (DFT+U) and London dispersion of the Grimme DFT-D type$^1$ to study the reactivity of VO$_x$/CeO$_2$(111) for ODH of benzyl alcohol (BA) to benzaldehyde (BAD) by using the VASP package$^{2,3}$. Elaborate calculations on various reaction pathways suggested that the oxidation of BA to BAD at monomeric VO$_x$/CeO$_2$(111) has remarkable catalytic activities, such as the low H-cleavage barriers. However, comparing with clean CeO$_2$(111), dimeric and trimeric VO$_x$/CeO$_2$(111) do not possess any improved activities. Detailed studies told us that these high activities of CeO$_2$ supported monomeric VO$_x$ originate from both structural and electronic effects. The three-dimensional monomeric VO$_x$ clusters sitting at surface can help to facilitate the H-cleavage. Especially, unique electronic 'hole' of monomeric VO$_x$ acts as some kind of magnet to seize the hydrogen from BA. These results may help us obtain a better view of ODH reactions, and facilitate design of more effective catalysts for similar reaction systems as well.

References


COLL 134

Self-assembled supramolecular nanotube yarn
In nature, especially with living organisms, the ordering structures can be detected at any dimensions. Thus, the macroscopic scale biomass not only contains supramolecular nanostructures, the ordering of structures also hierarchically run through the macroscopic scale with diverse expressional forms. For chemistry, however, it is still very difficult to construct artificial soft matters having both microscopic ordering and hierarchically organized structures throughout the macroscopic scale.

Here we report the first macroscopic supramolecular nanotube yarns directly spun from the diluted aqueous solution. We have found that an L-histidine terminated bolaamphiphile could self-assemble into ultra-long supramolecular nanotubes in slightly alkaline aqueous solution (pH 8-9). By automatic spinning process, such solution can be spun into bundled nanotube yarns with lengths in meter-scale and diameters of 1.5-5 µm at a large yield. Although the yarns are built totally via non-covalent interaction, they showed nominal tensile strength of 45-60 MPa with Young’s modulus coming to 6.8-9.9 GPa, which could be comparable to many covalent-linked polymers. Furthermore, porphyrin solution can move more than 1 centimetre along the vacuum dried supramolecular nanotube yarns, indicating the mass transportation through the macroscopic bundled tubular structures. These results provided the new horizon of hierarchical self-assembly and the continuous spinning of microscopic yarns from the solution of self-assembled small amphiphilic molecules opens a new strategy for building the nanoscale assemblies into ordered macroscopic supramolecular materials.
Synthesis of Au/Pd octopods by seed-mediated co-reduction: The influence of seed size and metal concentration

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Nanoscience research has become a diverse and prominent field that has applications in many different disciplines on account of the size-dependent characteristics of solids. Bimetallic nanoparticles combine the properties of diverse elements to create multifunctional structures that can have interesting optical and catalytic properties. However, particle morphology is often difficult to control using traditional synthetic methods. Seed mediated co-reduction, a method developed in the Skrabalak lab, addresses this challenge by simultaneously reducing two metal precursors in order to deposit metal onto a small nanostructure, a seed, to produce a desired shape. In this experiment the seeds were Pd nanocubes, with Au and Pd co-reduced to deposit both metals onto the nanostructures. The final results are Au/Pd octopods with eight branches where one branch grows out of each vertex of the nanocube seeds. Although many parameters within this synthesis are well studied, the upper limit of size control is not well established. By changing two parameters: the size of the Pd seeds and the amount of Au/Pd precursors added, octopods of different sizes and branch lengths were synthesized. Through the process of examining the products by electron microscopy and their optical properties by UV-visible spectroscopy, the designing of functional bimetallic nanocrystals can be improved in the future.

Synthesis and characterization of Pd ultrathin nanowires

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We will present a facile synthesis of ultrathin, five-fold twinned Pd nanowires in a polyol system and an in-depth understanding of the mechanism. Our studies showed that very slow reaction kinetics and an effective capping agent are the two key factors necessary for the successful synthesis of five-fold twinned Pd nanowires. In addition, Pd nano-bipyramids and nanocubes were also selectively synthesized by manipulating the reaction kinetics. It was found that the Pd nanowires evolved into multi-twinned Pd nanoparticles if the reaction time was extended from 1 to 4 h. The oxidative etching reaction was revealed to be responsible for the distinct shape evolution by creating instabilities within the Pd nanowires. The as-prepared Pd nanowires were used as electrochemical catalysts to evaluate the catalytic activity towards formic acid oxidation, with a resultant current density 3.1 times higher than that of the commercial Pd/C. This
work not only provides a facile synthetic strategy for the preparation of ultrathin Pd nanowires but also offers an in-depth understanding of the synthesis by elucidating the roles of oxidative etching, reaction kinetics, and capping agent in the synthesis.

**COLL 137**

**Oxidative etching and regrowth of Pd nanocrystals with different shapes and twin structures**

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We present a systematic study on the oxidative etching and regrowth of Pd nanocrystals, including single-crystal cubes bounded by \{100\} facets, single-crystal octahedra and tetrahedra enclosed by \{111\} facets, and multiple-twinned icosahedra covered by \{111\} facets. Owing to oxidative etching, Pd atoms were preferentially removed from the corners due to the passivation of \{100\} side faces of the nanocubes by Br\(^{-}\) ions and the lower surface free energy of \{111\} facets. The newly formed Pd\(^{2+}\) ions could be reduced and deposited back onto the high-energy sites (\{100\} facets and/or twin regions). The etching and regrowth rates could be controlled by simply varying the amount of HCl added into the reaction solution. For example, as the amount of HCl increased, Pd nanocubes were transformed into octahedra with smaller sizes. Unlike the case of Pd nanocubes, Pd octahedra were transformed into truncated octahedra, cuboctahedra, and spheres. Pd tetrahedra were transformed into truncated tetrahedra, and spheres. Pd icosahedra involved with twin defects were transformed into asymmetric icosahedra, flower icosahedra, and spheres. This work advances our understanding of the oxidative etching of Pd nanocrystals with various shapes and twin structures and offers a powerful means for controlling the shape and size of metal nanocrystals.

**COLL 138**

**Facile synthesis of Pd-Cu bimetallic tripods and their use as catalysts for formic acid oxidation**

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We will present our recent study on a Cu-assisted synthesis of Pd-Cu bimetallic tripods with purity higher than 90%. The tripods have high-density surface steps on their highly accessible surfaces and the arms were shown to grow along three \{211\} directions. We have confirmed that the tripods were made of a Pd-Cu alloy through XRD and EDS analysis. We systematically investigated the role of Cu in the formation of the tripod structure. The incorporation of Cu in the tripods was caused by the formation of Cu UPD layer on the Pd seeds since the tripods evolved from plate-like seeds with stacking
faults or twin planes. We also found that KBr played a key role in the overgrowth of triangular seeds to tripods. The Br⁻ ions could strongly bind to the three (100) side surfaces of triangular plates, forcing the Pd atoms to deposit on the three corners of the plate-like seeds to generate the tripods. When compared with the commercial Pd black catalyst, the Pd-Cu tripods exhibited substantially enhanced (eight times per unit mass of Pd) catalytic activity toward the electro-oxidation of formic acid. This study demonstrates a new way to overcome the high free energy of plate-like seeds and it provided a new direction for the synthesis of nanocrystals with plat-like or plate-evolved morphologies.

**COLL 139**

**Development of fragmented nanosheets and patchwork coating as aqueous surface modifiers for biomedical applications**

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Free-standing ultra-thin films (often called nanosheets) composed of biocompatible polymers (size >cm, thickness <100 nm) represent unique properties as good adhesiveness, exquisite flexibility, and a high degree of transparency¹). However, they are often hard to coat irregular/uneven interfaces due to the structural aspect (cm-size). In this paper, we propose a novel nanobiomaterial “fragmented nanosheets” to effectively coat the uneven interfaces and a patchwork coating as an aqueous surface modifier for biomedical applications.

Free-standing nanosheets composed of biodegradable poly(L-lactic acid) (PLLA) with a thickness of 60 ± 6 nm were successfully mass-produced by a simple combination of a spin-coating-assisted multi-layering process of poly(vinyl alcohol) and PLLA and a peeling technique. Intriguingly, the PLLA nanosheets could be easily fragmented by homogenization at 30,000 rpm and then reconstructed into a sheet on various interfaces (steels, glasses, plastics and skin) without any adhesive reagents. The adhesion behavior resembled a “patchwork”, which was evident as a sequential series of structural colors on the substrate. For a biomedical application, we demonstrated that the patchwork coating of fragmented nanosheets acts as an excellent barrier against burn wound infections by *Pseudomonas aeruginosa*². This material thus constitutes a promising alternative to conventional therapy for burn patients. We will also propose that the patchwork coating of other biocompatible polymers (polyimide and polyurethane etc.) containing phospholipid moiety³) converts various substrates to blood-compatible surfaces.

**COLL 140**

Asymmetric and symmetric bolaform supra-amphiphiles: The formation of imine bond influenced by aggregation

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Supra-amphiphiles refer to the amphiphiles fabricated by non-covalent interactions or dynamic covalent bonds. The amphiphility of supra-amphiphiles are very easy to modulate, therefore they are very useful tool for controlled self-assembly and disassembly and play a very important role in colloid and surface chemistry. Here we introduce a series of bolaform supra-amphiphiles with different symmetries on the basis of dynamic covalent bonds. It can be found that the supra-amphiphiles with a poorer symmetry always exhibit a lower imine formation at a given pH. The varied extents of imine bond formation indicate the different aggregations of these supra-amphiphiles, which are controlled by the molecular symmetry of the supra-amphiphiles. This research develops a simple path to fabricate asymmetric supra-amphiphiles and reveals that the aggregation of the supra-amphiphiles gives a “feedback” to the supramolecular linkage, which is quite similar with some mechanisms in biological system.

**COLL 141**

Nanoparticles trapped in fibers of unfolded proteins

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We have found that several, commercially-available proteins can, on their own, bring about biomineralization of gold nanoparticles. Each unique protein induces different morphologies (0-D shape and 1-D fiber/2-D mesh formation). We observe a distinct cutoff between the production of 0-D nanoparticles and the production of 1-D fibers/2-D mesh networks formed when the ratio of protein to gold is altered. This cutoff ratio is different for each individual protein. In this poster, we discuss the protein properties (molecular weight, structure, and pI) that lead to the observed effects. We also study the thermodynamics of the conversion of suspended nanoparticles into fibers as a function
of: ionic strength, chelator concentration, and pH. Finally, this poster details our efforts to use similar biomineralization protocols to produce: artificial tissue scaffolds, quantum dots, magnetic hydrogels, and functional enzyme nanocomposites.

**COLL 142**

**Functional ellipsoidal nanoparticles via block copolymer/homopolymer blends**

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Nature is a well of inspiration for chemists and materials scientists, especially when nano materials are considered. The major requirements in the synthetic formation of nature-inspired nano materials are predominantly shape anisotropy, stimuli responsiveness, spatially control over internal chemistry as well as nanostructured morphology. We have previously demonstrated that polymeric ellipsoidal nanoparticles with axially stacked lamellae are a particularly good example for synthetic nano materials. These particles are readily accessible via solvent evaporation in block copolymer/mixed surfactant systems.
As a result, shape anisotropy and internal axially stacked lamellar morphology are achieved in a facile way via block copolymer microphase separation. Since a broad range of polymer types are available, this concept offers a new platform allowing introduction of stimuli responsiveness and functionality.

In this contribution, an extension to the existing preparation method is described that utilizes homopolymer/block copolymer blends in the fabrication of shape anisotropic particles. The incorporation of homopolymers of both polymer types in stoichiometric ratio offers several advantages over the existing methodology with regard to tuning the final material's properties. Firstly, the domain spacing increases via homopolymer addition. Thus, precise tuning of the lamellae thickness is possible. Secondly, the addition of functionalized homopolymers allows for the incorporation of such chemical functionalities as crosslinkable moieties in the respective domains. This modular approach is a key factor with regard to selectively adjusting the material's properties to a specific application.

COLL 143

Visible light photocatalysis using C-doped TiO₂ derived from TiC: Effects of surface chemistry on photocatalytic activity

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Visible-light photocatalysts were prepared from TiC to create substitutional doped TiO₂ of controlled carbon content. The conversion from TiC to c-doped TiO₂ was monitored by **in-situ** X-ray diffraction and its bulk and surface compositions characterized by XRF, XPS and ToF-SIMS. The surface chemistry was further analyzed by FTIR and micro-Raman. The study established that the band gap can be deliberately shifted towards visible-light enabling activity tests on samples of discrete band gaps. Furthermore, the photocatalyst samples has relatively clean surface free of carbonaceous deposits. To investigate the role of surface chemistry on photocatalytic reaction, surface functionalities were introduced by grafting organic moieties with -COOH, -COH and –OH groups. The photocatalytic reaction was investigated for three model pollutants, a dye molecule (i.e., methylene blue), a refractory chemical (i.e., 1,2-dichlorophenol) and an endocrine disrupting compounds (i.e., dichlofenac sodium). C-doped TiO₂ without surface functionalization is active only for methylene blue, but not for the two colorless pollutants (i.e., 1,2-chlorophenol and diclofenac sodium). Selectively introducing the –COOH, -COH and –OH functional moieties showed significant improvement in visible-light photocatalytic activity for all three pollutants. The surface functional moieties are
believed to enhance surface hydrophilicity and improve OH\(^{-}\) generation, while simultaneously retarding electron-hole recombination.

**COLL 144**

**Imaging pericellular enzyme-instructed self-assembly of small molecules on live cells**

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As a universal phenomenon, the self-assembly of proteins or small molecules to form nanofibrils in a cellular environment is indispensable for the well-being of cells. There have been reports about the spatiotemporal distribution of fluorescent small molecules instructed by the enzymatic process in an intracellular environment. However, due to the complexity of live cells, selective formation of xenogenous nanofibrils on mammalian cells gains little attention. Here we report a method to image enzyme-triggered self-assembly of small molecules in pericellular space, especially of cancer cells that overexpress phosphatases. After conjugating a fluorophore to a small D-peptide derivative with a phosphorylated tyrosine motif, we found that surface and secretory phosphatases of live cells would dephosphorylate this precursor to trigger the self-assembly of the hydrogelator and result in pericellular nanofibrils. This enzymatic procedure not only generates a reaction product (i.e., nanofibrils of hydrogelators) that is both intensely fluorescent and highly photo-stable, but also reveals the regional heterogeneity of pericellular enzymatic activity. Thus, combining fluorescent imaging and enzyme-instructed self-assembly of small D-peptide derivative in a cellular environment, this approach allows the evaluation of pericellular self-assembly, the selectivity, the dynamics and the localization of the nanofibrils outside the live cells, as well as the characterization of the activities of surface and secretory phosphatases of live cells.
Efficient cross-linking strategies in colloidal crystal films featuring enhanced photonic and mechanical properties

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Photonic band gap materials attracted a great deal of attention as potential candidates for various optoelectronic applications.¹ Within this field, elastomeric polymer-based colloidal crystals, also referred to as synthetic opal films, show a reversible mechanochromic response while stretching with excellent color changes.²,³ The lack of mechanical strength in such opal films, which is a basic prerequisite for a reversible combined optical and mechanical response, can be overcome by subsequent photo- or thermally induced cross-linking reactions.³,⁴ However, cross-linking processes are necessary which reliably do not proceed under the conditions of colloidal crystallization and compression molding but which can be activated a posteriori. Within this contribution an in-situ cross-linked network, generated by subsequent UV irradiation of the melt-flow opal films as well as a thermally induced cross-linking protocol is described. Efficient reactions for thermally induced cross-linking are based on the chemistry of epoxides, alcohols and isocyanates. Monomers bearing the corresponding epoxide and alcohol functionalities were introduced into the seeded emulsion polymerization in order to obtain monodisperse particles with diameters in the range of 100-500 nm. As a result, the combined mechanical and optical properties of the opal films can be significantly improved. Studying the mechanical properties of these novel elastomeric opal films together with investigations of the excellent optical properties revealed that original iridescent reflection colors can be achieved after stretch-tuning and relaxation.

Study of optical and structural properties of magnetic fluids

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In this work, morphological, structural, magnetic and optical investigations were performed in iron oxide nanoparticles synthesized by chemical methods. Our goal was to correlate the synthesis parameters to the characteristics of the produced particles to improve their quality when compared to commercial samples. Superparamagnetic iron oxide nanoparticles (SPIONs) currently have a surge of interest as their potential has been demonstrated in many applications such as biomedicine, modern technology, diagnostics and molecular biology, among others. Therefore, the functionalization of these particles is a crucial step for these applications. The samples are fluid magnetic (SPIONs) commercial and synthesized by co-precipitation of metal salts in aqueous solution and the thermal decomposition of organometalic precursor with different coatings. These systems were characterized by transmission electron microscopy, X-ray diffraction, UV-Vis spectroscopy, magnetic measurements, Z-Scan technique (thermal diffusivity, nonlinear refractive index), thermo-optic coefficient and thermal conductivity. The results showed that nanoparticles synthesized by the co-precipitation method present advantage over the commercial samples, once they have the less size distribution. Through thermal decomposition of Fe(acac)₃, particles with narrower size distribution were produced. The synthesized samples showed better responses to the characterizations, mainly due to its size, which was about five times lower than the commercials. We are in debt to FAPESP, CNPq and Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos (INCT-FCx) for financial support.

Chemical analysis of fluids at the solid surface: Testing the complete slip boundary condition

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A fluid's flow profile near a solid surface directly impacts performance of devices across a wide spectrum of industrial, commercial, and research applications. Chemical and physical interactions combine to influence molecular scale slip and flow of fluids at solid surfaces. Hydrodynamic theory states that when a fluid contacts an ultra-smooth surface (< 5-7 nm RMS roughness), partial to complete slip boundaries can be achieved. However chemical forces also play a non-innocent role in forming these interfaces. In this work, we combine an innovative sampling technique with analytical spectroscopic measurements to experimentally investigate thin fluid films in this arena. We examine thin molecular fluid films supported on substrates designed with various
surface chemistries and roughness values between 1 and 30 nm RMS (as measured by Atomic Force Microscopy). Ellipsometry and vibrational spectroscopy measurements provide data for analysis of thickness and chemical structure of the fluid films.

**COLL 148**

**Systematic modulation of the mesoporous silica nanoparticle platform to improve in vivo performance toward clinical applications**

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Over the past decade, mesoporous silica nanoparticles have emerged as a highly versatile platform for dynamic drug delivery applications in cancer research. The literature has recorded all varieties of gating strategies, ranging from well establish biodegradable polymer systems to the use of supramolecular gating technologies for on command release of chemotherapeutics. There are currently limited examples, however, of this technology migrating from proof of principle studies into the clinic. To transition from academic to viable therapeutic applications, research into some of the fundamental elements of drug delivery must be investigated to produce a highly versatile, robust and effective platform for the *in vivo* environment. In our current investigations, we are building upon our past research with nano-gating technologies to improve upon the performance and adaptability of mesoporous silica in order to evaluate the technology towards chemotherapeutic drug delivery in an *in vivo* environment. We report the development of nano-gating systems in conjunction with the sol gel particle preparation methods and adaptive surface chemistry techniques to develop an array of materials to be tested *in vitro* for reliability and effectiveness.

**COLL 149**

**Preparation of chitosan microparticles having calcium carbonate shell via soft chemical process**

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Soft chemical process becomes of interest in recent years, since it is an energy-saving process carried out in the condition at ordinary temperatures and pressures. In this study, chitosan particles having a hard shell of calcium carbonate was prepared via a soft chemical process, which was called as biomineralization. If chitosan microparticles are coated with inorganic materials, the composite particles can be applied to microcapsules for a drug delivery system. Chitosan core particles were prepared by a dispersion neutralization method. The prepared particles were observed by SEM, and
average diameter of the particle was 14 micron. The chitosan microparticles were introduced into a supersaturated aqueous solution of calcium carbonate for one day. The resulting white precipitate was filtered off and dried in vacuo. SEM observation of the obtained powder was carried out and it was clarified that there were spherical microparticles whose average diameter was larger than that of chitosan core particle. And XRD peaks assigned to crystalline calcium carbonate were detected from the composite particles. These results indicated that the chitosan core particle was uniformly coated with calcium carbonate.

**COLL 150**

**Catalytic ozonation of EDC in a membrane reactor**

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A large number of chemical compounds in household products are known or suspected to be endocrine disruptor and their increasing presence in municipal waste water is alarming as conventional wastewater treatment processes are proven to be ineffective in treating these compounds. This work investigates an alternate technology that combines the three most effective processes for EDC treatment that include ozonation, adsorption and membrane separation in a single compact unit. The advanced ozone membrane reactor (AOMR) uses membranes for ozone distribution, reaction contactor and water separator to maximize EDC conversion and ozone utilization. Adsorbent was employed to trap the EDC and its byproduct in the reaction zone to achieve deeper oxidation. The use of catalyst and in particular Fe/C catalysts in a catalytic ozone membrane reactor (COMR) to speed up the reaction was also investigated. Both AOMR and COMR can achieve complete conversions of diclofenac sodium, caffeine and phthalates within 5 min residence time, but COMR can achieve a higher TOC removal of 70 % compared to AOMR (40 %).

**COLL 151**

**Novel graphene-wrapped TiO₂ nanofibers with effective interfacial coupling as ultrafast electron transfer bridges**

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For TiO₂-based photoanodes, the interfacial coupling between TiO₂ and conductive materials (e.g., carbon), plays a vital role in determining the electron transfer efficiency
and thus photoelectrical performance. In this paper, we describe a facile approach to effectively engineering the interfacial coupling between reduced graphene oxide (RGO) and TiO$_2$ in well-designed one-dimensional (1D) RGO-wrapped TiO$_2$ nanofibers, which act as ultrafast electron transfer bridges when implanted in photoanodes. The 3-5 nm RGO nanoshells were hybridized with TiO$_2$ nanofibers as an electron donor component via $d$-$\pi$ electron orbital overlap between C and Ti atoms, by adopting a thermal reduction at 450 °C. Remarkable photoelectric improvement in term of high photocurrent density by 2.2-fold and ultralow charge transfer resistance ($R_{ct}$) by 0.2-fold is ascribed to the interfacial charge transfer. Completely reduced RGO in RGO/TiO$_2$ nanofibers was not necessary at the expense of their hydrophilicity, as it led to unexpected isolation in the photoanodes. The thermal reduction temperature of RGO/TiO$_2$ nanofibers was found to be critical, and a maximal photocurrent density could be achieved by 2.7-fold at 530 °C. The excessive RGO/TiO$_2$ nanofibers more than 5 wt % had degrading effect on photoelectrical activity, largely due to the light-block effect and isolation in matrix. This strategy provides new insight for tuning intrinsically chemical and/or physical properties of well-designed semiconductor nanostructures with promising photoactivities in highly efficient photovoltaic devices.

**COLL 152**

**Functionalized graphene oxide drug delivery system as the unmodified paclitaxel carrier**

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Poor solubility of water-insoluble drugs in aqueous solution can be a critical limitation to oral absorption therefore has hampered their use for disease treatments. In this work, a novel anti-cancer drug delivery system consisting of functionalized graphene oxide (GO)
nanosheets and electrospray biocompatible gelatin nanospheres have been successfully developed. The chemical functionalization of GO by hydroxypropyl beta cyclodextrin (HPCD) were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectrum and high performance liquid chromatography (HPLC). The drug loading content (DLC) and drug loading efficiency (DLE) of Paclitaxel (PTX) included in HPCD were as high as 0.103 μg/mg and 59.5 %, respectively. The resulted PTX-GO-gelatin electrospray nanospheres were uniform in sizes of 200-500 nm. The concentration of gelatin in electrospray solution was found to be a key of generating the excellent nanospheres. Finally the in-vitro release profiles of PTX in the desired drug delivery system have been systematically investigated. The slow and smooth PTX release mechanism was discussed also.

Facile synthesis of versatile graphene quantum dots with tunable nitrogen-doping

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This paper reported a facile fabrication of N-doped graphene quantum dots (N-GQDs) which showed controllable chemical properties through a hydrothermal treatment. The N-GQDs had a uniform size of 3.06±0.78 nm and preferred the equilibrium shapes of circle and ellipse due to the minimization of edge free energy. The N/C atomic ratio of N-GQDs could be precisely tailored in a range of 8.3 at. % to 15.8 at. % by simply controlling the concentration of N source (ammonium hydroxide, NH4OH). The N dopants either formed pyrrolic structure or substituted the C atoms in graphene lattices, consequently allowing the N-GQDs with a significant enhancement in
photoluminescence quantum yield of 34.5 % and radiative rate constant ($\kappa_r$) of $7.93 \times 10^7$ s$^{-1}$. The N-GQDs were further found to be suitable as photocurrent conversion materials due to benign energy matching with anatase nanofibers, the ultrafast electron injection at their interface, and efficient electron transfer. This work provides an efficient and inspiring approach to engineering both chemical components and physical properties of N-GQDs, and will therefore promote their basic research and applications in energy conversion.

Interfacial self-assembly: A novel and facile strategy for nanofilm and nanodevice fabrication

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Since discovered in 2004, oil-water interfacial self-assembly of nanostructures has become a novel strategy for fabrication of nanofilms.[1] It is a powerful bottom-up approach for the film fabrication due to low cost and high efficiency, and is simply and universal for almost all low-dimensional nanostructures. The most prominent advantages of this assembly strategy are its simplicity and universality for almost all low-dimensional nanostructures. Furthermore, the quality of the as-assembled nanofilms should be high enough for the optoelectronic or electronic device applications. Herein, we present our present work on nanofilm and nanodevice fabrication from this novel and low-cost strategy. High quality rare-earth luminescent nanofilms and high quality semiconducting nanofilm-based photodetectors have successfully fabricated.[2,3] The photodetectors constructed from this facile method shows good sensitivity, excellent stability and fast response time, which are quite
promising for applications such as optical communications, flame sensing, missile launch.

Furthermore, we have fabricated a high-performance CoO nanofilm-based electrical resistive switching device from this self-assembly method [4]. A gigantic change in resistance induced by external electric field has been observed, and a very fast switching between the high resistance state (OFF) and low resistance state (ON) in ns level has also been realized for this device. This novel and facile strategy significantly decreases the cost of fabrication procedure, and can also be extended to fabricate other inorganic semiconductor thin-film photodectors and field effect transistors (FETs) [5].

References:


Structural analysis of micelles formed by calix[4]arene lipids bearing quaternized amine

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Structure formation through self-assembly is one of the interesting phenomena in supramolecular chemistry. We synthesized a calixarene lipid bearing four amine head groups (Figure1. Cal3) and found that Cal3 formed a regular polyhedron structure micelle (cubic symmetry) only in acidic conditions.

To obtain such a polyhedron structure in neutral condition, we synthesized two amphiphilic calix[4]arene bearing quaternary amine(QA3 and QA5) and explored pH dependence of detailed structure of QAXs by using of small-angle X-ray scattering(SAXS).Figure2 shows the SAXS profiles of all samples at different pHs.
This shows that QAXs are not pH-responsive structural changes and formed micelles in a neutral pH. In addition, aggregation number of QA3 is 8, and QA5 is 12. The results indicate that QAXs formed regular polyhedron structure micelles.

**COLL 156**

**Influence of humic substances and biomacromolecules on MnO2 colloidal aggregation kinetics**

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In this work, the early stage aggregation kinetics of manganese dioxide (MnO2) colloids in aqueous solution and the effects of constituents of natural organic matter (i.e., Suwannee River fulvic acid (SRFA), Suwannee River humic acid (SRHA), alginate, and bovine serum albumin (BSA)) were investigated by time-resolved dynamic light scattering. MnO2 colloids were significantly aggregated in the presence of monovalent and divalent cations. The critical coagulation concentrations were 28, 0.8, and 0.45 mM for NaNO3, Mg(NO3)2, and Ca(NO3)2, respectively. The Hamaker constant of MnO2 colloids in aqueous solution was 7.84×10^-20 J. All the macromolecules tested slowed MnO2 colloidal aggregation rates greatly. The steric repulsive forces, originated from organic layers adsorbed on MnO2 colloidal surfaces, may be mainly responsible for their stabilizing effects. However, the complexes formed by alginate and Ca^{2+} (>5 mM) might play a bridging role and thus enhanced MnO2 colloidal aggregation instead. These results may be important for assessing the fate and transport of MnO2 colloids and associated contaminants.
Zeta potential for determination of pKa values of multilayered 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’s): poly(4-vinylphenol) (PVPh), poly(norbornenylhexafluoroisopropylmethyl alchol) (HFIPA), and recently poly(4-vinylbenzenecboronic acid) (PVBBA). These pPE’s have pKa values in the basic versus acidic pH range. We are using zeta potentials to accurately determine the pKa values of these polymers once multilayered with the weak polyelectrolyte, poly(allylamine hydrochloride) (PAH). For example, with PAH there is an increase in pKa_{(app)} as layer number increases with a plateauing nearing 11.0 for a PAH/PVPh system assembled at pH 11.0. For PVPh assembled under the same conditions, there is also an increase in pKa_{(app)} as layer number increases with a plateauing nearing 11.4.

Size matters: The effect of tip width and branch length on plasmonic properties of stellated, bimetallic nanocrystals
Metallic nanocrystals (NCs) have tunable plasmonic properties that depend on their size, shape, composition, and local environment. Such properties enable the use of NCs in applications that range from medical therapies to sensors. Assembly of these metallic NCs into large-scaled materials that retain or propagate the properties of the individual NCs is of great interest. For example, bimetallic NCs can be assembled to create multifunctional plasmonic platforms such as refractive index (RI)-based sensor arrays. Here, branched bimetallic Au-Pd NCs are synthesized and their optical properties characterized at a single particle level. Small changes in NC features can significantly affect the plasmonic response; such effects are hidden in ensemble measurements which creates a need to thoroughly characterize the plasmonic response of these single NC “building blocks”. Correlation of the structural features of these branched bimetallic NCs with their optical properties has been achieved via scanning electron microscopy (SEM) with darkfield scattering spectroscopy. By determining the effect of individual NC features on the plasmonic response, guidelines for the rational design of new multifunctional plasmonic platforms should be achieved.

COLL 159

Surfactant-assisted preparation of $\alpha$-Fe$_2$O$_3$/TiO$_2$ composites and their catalytic activities

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Nano-sized $\alpha$-Fe$_2$O$_3$ particles were grafted on the surface of TiO$_2$ by using facile surfactant assisted preparation method. After calcination at 450 ºC, the crystal structures were hematite and anatase mixed phase. The thickness of $\alpha$-Fe$_2$O$_3$ shell could be controlled by changing the concentration Fe salt and the stable shell could be formed by using CTAB. The composite were analyzed by using TEM, EDS, XRD, XPS, VSM and PL. As an application of prepared composites for water treatment, their catalytic performances for the degradation of methylene blue were examined by using UV-Vis spectrophotometer under room light irradiation. The $\alpha$-Fe$_2$O$_3$/TiO$_2$ composites prepared by using 25 mmol of Fe salt with CTAB showed the highest performance of MB degradation because of effects of Schottky barrier and band edge shift contributed to formation of Fe$_2$O$_3$ nanoparticles on TiO$_2$ surface.

COLL 160

Formation and characterization of hematite-based nanocomposites prepared in surfactant/cosurfactant system
Hematite-based nanocomposites were synthesized using iron (II) chloride, cetyltrimethylammonium bromide (CTAB) as a surfactant and tert-butanol as a cosurfactant. Silica and sulfonate-functionalized polystyrene (PS) were used as hard template materials. Under basic condition which was regulated by ammonium hydroxide, ferrous ions reacted with hydroxide ions, and iron hydroxide nuclei and particles which were stabilized by CTAB molecules were formed. The electrostatic interaction between negatively charged core and the particles surrounded by cationic surfactant induced iron compounds to be immobilized onto the surface of spherical templates. In the case of silica-hematite composite preparation, additional calcination was needed in the final step to unify iron compound with multi phase into hematite. In this study, we estimated morphology, crystallinity, BET surface area and so on according to the variation in the iron salt and surfactant quantities. In addition, adsorption properties of samples were examined through methylene blue (MB) adsorption using UV-vis spectroscopy.

COLL 161

Facile synthesis of uniform nonspherical polymeric colloidal particles

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Nonspherical latex particles are of great interest in the field of colloids and materials science. However, the shape control of latex particles has been a key challenge for material scientists since the surface tension prioritizes formation of spherical particles for minimizing the surface energy. Traditional polymerization method involves precise control of the experimental conditions, including the cross-linking density of seed latex, swelling, feeding mode of cross-linker and polymerization time[1,2]. Herein, we report a facile method to prepare nonspherical amphiphilic random copolymer of poly(styrene-co-methacrylic acid) (poly(St-co-PMAA)) colloidal particles with well-defined shapes and high yields by varying the molar ratio of styrene (St) to methacrylic acid (MAA) based on emulsifier-free polymerization. In our strategy, no seeds, no cross-linker, and no multi-step control were needed. Due to the presence of carboxyl groups, these colloidal particles can be used as templates for fabricating core-shell nonspherical functional materials, such as poly(St-co-PMAA)@SiO₂, poly(St-co-PMAA)@polypyrrole). The corresponding hollow structures (SiO₂ and Polypyrrole) could be obtained after removal of the templates.
Figure 1. SEM images of nonspherical particles. A) poly(St-co-PMAA), B) poly(St-co-PMAA)@SiO2; C) poly(St-co-PMAA)@polypyrrole. TEM images of the corresponding hollow particles in the inset, scale bar: 100nm.

References:


COLL 162

Formation of insulator oxide films by acid catalyzed hydrolysis of metal alkoxides in supercritical fluid carbon dioxide

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Metal oxide films can be produced by hydrolysis of metal alkoxide precursors in the presence of an acid catalyst in supercritical fluid carbon dioxide. In this study, a new process has been developed to encapsulate PbS films with SiO2. Tetraethyloorthosilicate (TEOS) as a precursor and acetic acid as a catalyst are used to form SiO2 films on
surfaces of different substrates. The SiO₂ film formation may be expressed by the following equation:

\[
\text{Si(OCH₂CH₃)}₄ + 2\text{H₂O} \xrightarrow{\text{acid}} \text{SiO₂} + 4\text{CH₃CH₂OH} \quad (1)
\]

Without the acid catalyst and at room temperature, hydrolysis of TEOS is very slow. When acetic acid is used as the catalyst, a smooth silicon dioxide film with reasonable thickness can be formed in supercritical fluid CO₂ at temperatures above 100 °C. The deposition reaction actually started at room temperature but produces good quality thick films at 100 °C. In the absence of acetic acid, only uneven and thin silicon dioxide films can be formed. The acid catalytic reaction probably involves proton coordination to the oxygen atoms of TEOS molecules that facilitates the hydrolysis. Water for hydrolysis is generated by the esterification process which can be written as

\[
\text{H₃C-COOH} + \text{C₂H₅OH} = \text{H₃C-COOC₂H₅} + \text{H₂O} \quad (2)
\]

Preliminary spectroscopic data of lead sulfide (PbS) nanoparticle arrays covered with SiO₂ films are given in this presentation.

COLL 163

Composition-controlled and uniform PtNi octahedra in oxygen reduction reaction and their theoretical study

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Uniform PtNi octahedra with different alloying composition, including Pt₁₈Ni₆, Pt₁₂Ni₁₂, and Pt₁₀Ni₁₄, are successfully prepared through fine-tuning the precursor ratio (Pt-to-Ni) in the presence of dioctyl amine (DiOL) and oleic acid (OAc). PtNi octahedra with different alloying composition have been well characterized via high-resolution transmission electron microscopy (HR-TEM) and powder x-ray diffraction (PXRD). The optimal surfactant ratio for DiOL versus OAc plays a key role in the formation of PtNi octahedral due to the specific crystal facet-surfactant bindings on the growth seed. Careful electrochemical examinations show that the oxygen reduction reaction (ORR) mass activity (MA) and specific area activity (SA) of all PtNi octahedra outperform those of commercial Pt/C catalysts. The results show that the MA of Pt₁₈Ni₆, Pt₁₀Ni₁₄, and Pt₁₂Ni₁₂ octahedra are ~1.7 folds, ~1.8 folds and ~2.1 folds, respectively, higher than that of the Pt/C catalyst. The SA of Pt₁₈Ni₆, Pt₁₀Ni₁₄, and Pt₁₂Ni₁₂ octahedra are ~2.9 folds, ~4.1 folds and ~4.3 folds, respectively, higher than that of Pt/C catalyst as well.
The plot of ORR enhancements as a function of the alloying composition of PtNi octahedra reveals a volcano-shaped plot, being maximized at equal molar ratio. Also, the volcano-shaped trend of ORR enhancements proves that Pt$_{12}$Ni$_{12}$ octahedra have the superior ORR activities. The results are firmly supported by theoretical works, concluding that the Pt$_{12}$Ni$_{12}$(111) surface provides larger adsorption energies for H, O, O$_2$, and OH species than those of Pt$_{18}$Ni$_6$(111) and Pt$_{10}$Ni$_{14}$(111) counterparts, whereas the molecularly adsorbed H$_2$O product is calculated to be the lowest in adsorption energy on the Pt$_{12}$Ni$_{12}$(111) surface. Subsequently, a combination study of chemical derivation and theoretical calculations is performed to gain in-depth insight into the ORR on Pt$_x$Ni$_{24-x}$(111) surfaces.

**COLL 164**

**Novel application of scaffold treatment procedure with minimum side effects by using an engineered biodegradable scaffold**

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This paper represents a scaffold implantation to serve as an alternative method to conventional therapies associated with negative side effects.

**COLL 165**

**Utilization of protein-based nanoparticles developed for hydrophilic coating as an interface modifier in the latex elastomer**

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Cyanoacrylate nanoparticles have been studied in great detail over the past three decades with a view to their use as controlled release drug delivery materials. They have been synthesized by dispersion polymerization in aqueous media. The mechanism of polymerization is anionic where the initiating species is the hydroxyl anion that was derived from dissociation of water.

For the preparation of nanoparticles to be used for hydrophilic coating, amine groups on the surface of protein molecules (from either an animal protein or cereal proteins) have been utilized as initiator for the polymerization. The resultant copolymer is amphiphilic in nature, and forms stable nanoparticle suspension. The suspension containing these nanoparticles shows an excellent coating capability on the surface of hydrophobic materials. A simple spray coating changes the wetting property of the material instantly and dramatically. When the coating is applied to solid surfaces like glass, it spreads out,
preventing the beading of water. This technology is applicable to the manufacturing of glass-window cleaners.

When a tiny amount (ca. 2%) of these nanoparticles are blended into latex particle suspensions, the mechanical properties of produced elastomers are prominently improved. This improvement is due to the interface-modifying effect of the nanoparticles since the incorporated nanoparticles are amphiphilic. The relationship between the mechanical property of final product and the structure of incorporated nanoparticle will be discussed.

COLL 166

Developing surface plasmon resonance (SPR) as a tool for measuring thermal denaturation profiles of hybridized DNA on surfaces

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Measurements of thermal denaturation profiles from DNA in aqueous solution (e.g., by UV absorption or DSC) have provided a foundation for understanding DNA thermodynamic properties. However, analytical techniques are underdeveloped for measuring these same properties for DNA that is immobilized on surfaces. We have recently developed three strategies that use surface plasmon resonance (SPR) imaging to obtain thermal denaturation profiles of hybridized DNA on surfaces. While SPR is a versatile tool for quantifying DNA hybridization activity, incorporating the temperature functionality needed to monitor DNA denaturation profiles presents numerous practical challenges. Specifically, variation in the refractive index of the contacting aqueous buffer solution with temperature results in large changes in the SPR resonance condition, which can overwhelm the analytical response from the DNA analyte.

One strategy we have developed is based on simply monitoring the shift in the SPR resonance wavelength as a function of the sensor temperature, while applying rigorous corrective measures to subtract out bulk solution effects. Quantitative results from this method of obtaining thermal denaturation profiles is compared to results from two alternative methods, which are both less reliant on these corrective measures: 1) Incrementally increasing the temperature of the SPR sensor and returning to the original sample temperature between increments, and 2) Applying a spatial temperature gradient across the sensor surface.

COLL 167

Core/shell electrospun hyaluronic acid/polycaprolactone nanofibrous membranes embedded with silver nanoparticles for dual antibacterial and antiperitendinous adhesive function
As one of the common complications after tendon injury and subsequent surgery, peritendinous adhesions could be minimized by directly placing a physical barrier between the injured site and the surrounding tissue. With an aim to solve the shortcomings of current biodegradable anti-adhesion barrier membranes, we propose to use a core/shell structured electrospun hyaluronic acid/polycaprolactone nanofibrous membrane embedded with silver nanoparticles (HA/PCL+Ag NFM) to prevent bacterial infection and peritendinous adhesions post tendon repair surgery. We use a coaxial electrospinning technique to fabricate core-shell nanofibers with HA in the core to exert a long-term anti-adhesion effect from the controlled release of HA, and PCL embedded with silver nanoparticle in the shell layer to increase the mechanical strength and to exert short-term anti-bacterial effect from released silver ions. For comparison, polycaprolactone nanofibrous membrane (PCL NFM), core/shell structured hyaluronic acid/polycaprolactone nanofibrous membrane (HA/PCL NFM) and HA/PCL+Ag NFM were prepared and analyzed by scanning electron microscopy, transmission electron microscopy, thermal gravimetric analysis, X-ray diffraction analysis, mechanical testing, and studied for controlled release of silver ions and HA. The average fiber diameter is not significantly different between the membranes. HA/PCL and HA/PCL+Ag nanofibers present a core-shell structure with silver nanoparticles shown in PCL sheath. TheNFMs are with microporous (0.87-2.16 μm) structure to effectively block penetration of adhesion-forming fibroblasts during tendon healing. Tensile testing shows the NFMs are robust with suitable mechanical properties for application by surgeons after surgery. From the release profiles, the release of silver ions is completed within four days while that of HA could be extended up to ten days, meeting the needs for short term antibacterial and long term anti-adhesion requirement after tendon surgery. Using agar diffusion test, the antibacterial activity of HA/PCL+Ag NFM could be confirmed. From in vitro cell culture experiments, the HA/PCL+Ag NFM is found to reduce fibroblast attachment and proliferation without showing significant cytotoxicity. In vivo studies with a rabbit flexor digitorum profundus tendon surgery model confirm the efficacy of HA/PCL+Ag NFM in reducing peritendinous adhesion compared with the control and other NFMs from gross observation, histology, joint flexion angle, gliding excursion and biomechanical evaluation. An injured tendon wrapped with HA/PCL+Ag NFM also showed the same tensile strength as a naturally healed tendon, indicating the anti-adhesion NFM does not compromise tendon healing.

COLL 168

Influence of the nanoparticle PEG corona on the affinity of targeting ligands

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The PEGylation of nanoparticles is one measure to diminish protein absorption to colloids and to sterically stabilize them. However, since the PEGylation also hampers nanoparticle-cell interactions, targeting ligands are attached to distal PEG chains. These foster and control the binding of nanoparticles to their target cells. Unfortunately, this PEGylation of a ligand can have unfavorable consequences for its target affinity. Using angiotensin II (Ang II), a ligand recently investigated for nanoparticular therapy of the infarcted heart [1], we determined to which extent its affinity is decreased upon PEGylation. Furthermore, we determined the ligand affinity when displayed by a multivalent nanoparticle.

Ang II was PEGylated at its N-terminal aspartic acid using an mPEG5k-NHS ester. For conjugating Ang II to nanoparticles, an N-terminal thiolated Ang II derivative was reacted with maleimide-activated PEGylated quantum dots to yield ligand-decorated nanoparticles. The affinity of Ang II, its PEGylated counterpart as well as the Ang II-modified nanoparticles was determined using intracellular calcium measurements with fura2-AM and rat mesangial cells. Here, native Ang II showed an EC₅₀ of 70.1 nM which dropped upon PEGylation by a factor of 4.5 to 320 nM. In contrast, nanoparticles decorated with Ang II regained an increased affinity of 8.9 nM. This greatly increased affinity can be attributed to a multi-ligand binding mechanism that nanoparticles can exhibit [2]. In addition, the nanoparticles showed strong cellular uptake as seen with confocal microscopy and flow cytometry.

We conclude that, although a ligand’s affinity can be decreased by PEGylation, the high avidity of nanoparticles can make up for this affinity loss and even surpass the affinity of the native ligand.


COLL 169

Spectroscopic investigation of the binding affinity of molecular dyes to metal oxide nanoparticles suspended in liquid medium

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Metal oxide nanoparticles (NPs) are an important class of nanomaterials that have found widespread application in the realm of energy conversion, catalysis, and pollution remediation methods. In particular, semiconducting oxide materials, such as zinc oxide (ZnO) and titanium dioxide (TiO₂) NPs, show excellent promise for the development of dye sensitized solar cells (DSSCs). DSSCs involve absorption of light by the molecules adsorbed at the surface of oxide NPs. One of the major obstacles to increase the efficiency of DSSCs is to obtain an optimum condition for the adsorbed dyes. To better understand the mechanism by which dye molecules adsorb to these nanoparticles, we
have utilized surface sensitive second harmonic generation (SHG) spectroscopy and measured adsorption isotherms of an array of dyes relevant to the development of DSSCs. Using SHG, the binding affinities of different molecules, such as eosin and coumarin dyes, onto ZnO and TiO2 NPs suspended in non-aqueous medium have been determined. Our investigation highlights the applicability of SHG in probing the adsorption of dyes to semiconducting NPs and provides insights into the nature of dye-particle surface interaction.

COLL 170

Generic approach to fabricate cluster-nanoparticle or single-nanoparticle based characterization

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Micellar encapsulation of nanoparticles using PEG-phospholipid is an efficient approach in converting hydrophobic nanoparticles to hydrophilic/biocompatible ones. For both magnetic nanoparticles (MNPs) and quantum dots (QDs), there are interests to fabricate cluster-nanoparticle micelles (CNMs) and/or single-nanoparticle micelles (SNMs). CNMs have a relative large hydrophobic core and get a flexibility to load drugs in the cores, while keeping magnetic moments or fluorescence for magnetic resonance imaging (MRI) or optical imaging. CNMs adopting MNPs also enhance magnetic relaxivity of micelles for MRI. SNMs would have smaller sizes compared to CNMs, which will benefit their cell/tissue uptake and thus enhance their bioavailability. Currently, the chloroform-based dry film method is the widely reported approach for the preparation of CNMs or SNMs. However, this method usually takes a long time to air-dry chloroform. Moreover, it involves heating or hot water for the film hydration, which may be incompatible with certain functional groups on the PEG end (e.g., maleimide). Recently, a dual solvent exchange method has been reported adopting both chloroform and DMSO. However, it is developed for SNM preparation and also involves additional solvent DMSO to increase cost and more experimental steps such as DMSO removal. There is lack of a simple and efficient method that can be adapted to fabricate either CNMs or SNMs. In this work, a capable method was developed for the fabrication of CNMs or SNMs. Briefly, a mixture of nanoparticles and PEG-phospholipid in THF is added into H2O under ultrasonication. By simply adjusting the mass ratio of nanoparticles to PEG-phospholipid, the sonication power and the mixture addition strategy, CNMs or SNMs of MNPs and QDs can be produced without slow air-dry, heating, or additional solvents. The produced CNMs or SNMs were characterized in terms of their sizes, optical properties, colloidal stability, and/or magnetic relaxivity (by MRI).
Tuning the helical nanostructure and supramolecular chirality by water in the organogels

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The self-assembly structure of a cationic amphiphile with pyridinium and multi-hydrogen bonding sites including urea and amide (PULG) are explored in various organic solvents. Although no gelation occurred in all tested organic solvents, the gel could be obtained when a small amount of water was introduced into a series of PULG organic dispersion, regardless of the water miscible or immiscible with these organic solvents. Through the gel formation, the molecular chirality of the amphiphile can be transferred to the supramolecular assemblies and nanostructures. It is observed that chirality of the supermolecules is sensitive to the polarity of solvent. Specifically, polar solvents induced M-chirality, while the nonpolar solvents induced P-chirality. More interestingly, the added water with different amount can tune the self-assembled nanostructures from fiber to the chiral twist with varying pitch length, and then unfold them to the platelet-like morphology. Our results suggest that water plays an important role in the gelation and tuning the helical assemblies through delicate synergistic balancing hydrophobic interactions and hydrogen bonding between water and PULG.

Real-time liquid crystal-based biosensor for urea detection

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A transmission electron microscopy (TEM) grid filled with 4-cyno-4-pentylbiphenyl (5CB) on the octadecyltrichloro silane-coated glass in an aqueous medium was developed to construct a urea biosensor by coating poly(acrylicacid-b-4-cynobiphenyl-4-oxyundecylacrylate) (PAA-b-LCP) at the aqueous/5CB interface and immobilizing urease covalently to the PAA chains. The urea was detected from a planar to homeotropic (P-H) orientational transition of 5CB by polarized optical microscopy under crossed polarizers. This TEM grid sensor with the maximum immobilization density of urease, 0.17 molecules/nm² enabled the detection of urea at concentrations as low as 5 mM by a P-H change with a half time of full P-H change of 250 seconds. This TEM grid sensor could detect urea in blood without inference of hemoglobin and ascorbic acid. This new and sensitive urea biosensor has the merits of low production cost and easy detection through the naked eye, and might be useful for screening the urea level in the human body.
Liposome-nanoparticle hybrids for combined cancer therapy applications

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Gold nanoparticles of diverse shapes and sizes have been proven as extremely useful tools in bioimaging and hyperthermal therapy applications. Meanwhile, liposomes are highly efficacious in the delivery of small molecules, peptides, and nucleic acids. In the current work, several liposome-nanoparticle hybrids have been developed, in which different shapes and sizes of plasmonic or magnetic-plasmonic nanoparticles have been encapsulated within slightly negatively-charged liposomes to yield the potential for synergistic therapeutic effects. Different targeted therapies will be demonstrated using different cancer cell lines by altering the targeting and chemotherapeutic components.

Mechanism of temperature dependent supramolecular fibrillization of small molecules

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Self-assembly occurs extensively in biological systems, ranging from cytoskeleton protein filaments in cells to dense plaques of fibrous inappropriately folded protein aggregates in brain tissue. Although the assemblies share the same nature of peptide and non-covalent interactions, they exhibit drastically different thermal stability. By mimicking the self-assembly behavior, a class of novel soft material/hydrogel, has been developed for a variety of biomedical applications ranging from 3-D cell cultures and stem cell differentiation to regenerative medicine, controlled drug delivery and tissue engineering. In previous studies relatively little attention has been paid to the thermodynamic behavior of the assemblies. For example, temperature dependence of the self-assembly of small molecules is largely unknown. Here we report on the temperature dependent self-assembly of typical hydrogelators using dynamic light scattering (DLS), NMR, and small angle neutron scattering (SANS). DLS yields information on the initial stage of fiber formation. SANS is used to determine the structural characteristics of these supramolecular assemblies (cross-sectional radius of the fibers, average mesh size of the network, etc.). We believe a better understanding of the self-assembly process will help us to design nanofibers/hydrogels for applications in biology and medicine.
**COLL 175**

**Spectroscopic study of polyoxometalates immobilized on light-absorbing nanoparticles for robust light-induced water oxidation**

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Light absorbing nanoparticles such as titanium dioxide, tungsten oxide, and hematite have been employed as supports for heterogenizing transition-metal-substituted polyoxometalate (POM) water oxidation catalysis (WOCs). These POM-based WOCs are known to be fast, selective, and oxidatively stable in their homogeneous phase. In heterogenized systems, such as on an electrode or other modified surfaces, distinguishing the durability and activity of the surface-bound POM versus leached homogeneous POM is challenging. In this study, $[\text{Ru}_4(\text{OH})_2(\text{H}_2\text{O})_2(\alpha-\text{XW}_{9}\text{O}_{34})_2]^{10-}$, where $\alpha=\text{Si}^{4+}$, and $\text{P}^{5+}$, have been immobilized on modified TiO$_2$, WO$_3$, and $\alpha$-Fe$_2$O$_3$ nanoparticles and found to retain catalytic water oxidation activity after multiple use cycles under conditions similar to the homogenous POM-catalyzed light-induced water oxidation system (photosensitizer and sacrificial oxidant). Replacing the photosensitizer with a light-absorbing nanoparticle support may provide a more direct and stable heterogenized system for catalytic water oxidation. The interaction between POM and nanoparticle surface before and after catalysis has been studied using spectroscopic and microscopic methods.

**COLL 176**

**Integrating gold nanoparticles with biomolecules through the oxidative coupling of anilines and aminophenols**

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There are a number of approaches to interface biomolecules with gold nanoparticles (AuNPs). Existing strategies include electrostatic absorption, chemisorption (taking advantage of the strong thiol-Au interaction), affinity-based non-covalent interactions (His-6/Ni-NTA, streptavidin/biotin interactions), and AuNP surface passivation followed by subsequent functionalization. These strategies, however, suffer from significant background absorption of the AuNPs to the biomolecules of interest. Established conditions also often require reagents that are unstable in aqueous solutions, harsh reaction conditions, and/or long reaction times. Our group has developed a rapid, chemoselective bioconjugation through the oxidative coupling of anilines and aminophenols. This reaction proceeds under mild conditions with fast reaction times. Progress towards adapting this oxidative coupling strategy to make well-defined and stable AuNP-bioconjugates will be discussed.
Characterization of highly porous titanium dioxide nanotubes and nanoflowers prepared via novel oxalate methodology

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A facile and novel method for the synthesis of hollow, low-density titanium dioxide (TiO₂) nanotubes (NT) and nanoflowers (NF) has been demonstrated using a hydrothermal sol-gel reaction in a pressure vessel. Titanium isopropoxide (TIPP), oxalic acid, and sodium hydroxide (NaOH) were selectively reacted to produce the desired TiO₂ morphologies. Bulk densities and porosities were measured using BET, confirming the hollow nature and the significantly reduced density of the NT. TEM analysis similarly supported the presence of the hollow NT. XRD analysis confirmed the crystalline polymorphs of the TiO₂ morphologies. UV/Vis spectra of the NF and NT products indicated interesting similarities and differences to commercially available porous titania products such as P25 and RCL-9.

Facile synthesis of Fe₃O₄-CuInS₂/ZnS magnetofluorescent nanoprobes and their characterization

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Magnetofluorescent nanoparticles, i.e. nanocomposites of magnetic nanoparticles (MP) and quantum dots (QDs), are of research interest due to their potential multimodal imaging applications. These particles can be used for both magnetic resonance (as contrast agents) and fluorescent imaging studies. Conventional approaches for magnetofluorescent nanoparticles mainly used chloroform-based dry film method and/or also adopt cadmium-based QDs. The dry film method takes a long time for particle fabrication, and cadmium-based QDs bring safety concerns for biological applications due to the high toxicity of cadmium. In this work, a fast and efficient method using THF/H₂O/ultrasonication and low toxicity near infrared CuInS₂/ZnS QDs was developed for the fabrication of magnetofluorescent nanoparticles. Briefly, a mixture of magnetic nanoparticles, quantum dots, and phospholipid in THF is added into H₂O under ultrasonication. Water-soluble phospholipid micelle encapsulated composite of both particles are formed. The produced samples were characterized in terms of their optical properties, colloidal stability, iron content, and magnetic relaxivity (by MRI). Although
fluorescence quenching was observed for the hybrid micelles, adequate fluorescence for optical imaging is still present. Samples are stable in the solvents/conditions tested within one or two weeks after preparation. High iron recovery (> 50%) was achieved for these hybrids. The magnetic relaxivities of these samples were measured to be from 126 mM⁻¹s⁻¹ to 215 mM⁻¹s⁻¹ depending on the mass ratio of starting materials (MP and QDs) for micelles preparation.

COLL 179

Halloysite as a nanoreactor for metal-organic framework

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The halloysite nanotube, obtained from deposited soil, has a cylindrical structure with a large surface area similar to a paper towel roll. The morphology of a multi-walled tubular HNT is analogous to that of multi-walled carbon. The halloysite is well known for its many applications as nanoreactors or nanotemplates, catalysts, and capillaries. In this study, the halloysite was exploited as a nanoreactor to synthesize well-known metal-organic framework (MOF), HKUST-1. Since this hybrid material mainly consists of the micropores, it can complement the mesoporosity of the halloysite which is the main porosity of it. Close packing of the lumen of the halloysite was confirmed by transmission electron microscopy (TEM), and scanning electron microscopy (SEM) was used to identify whether the isolated MOF crystal exists. Fourier-transform infrared spectroscopy (FT-IR) was used to find functionalities, and the crystallinity of the product was identified by X-ray diffractometry (XRD). Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods indicated that the lumen of the halloysite was packed, with the crystal having specific micropores of the HKUST-1.

COLL 180

Synthesis and characterization of well-ordered methyl-, ethynyl-, and propynyl-terminated Si(111) surfaces

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Alkyl-termination of Si(111) surfaces has been shown to effectively passivate the surface to oxidation in air. Methyl groups are unique among saturated hydrocarbons in that they are capable of terminating nearly all of the Si(111) atop sites. However, secondary functionalization of methyl-terminated Si has proven challenging. Ethynyl and propynyl groups, which have Van der Waals radii similar to methyl groups, contain functional groups capable of secondary reactivity. Thus, ethynyl- and propynyl-terminated Si(111) surfaces were prepared by a two-step halogenation/alkylation procedure and characterized by transmission infrared spectroscopy (TIRS), X-ray
photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy
(HREELS), low energy electron diffraction (LEED), atomic force microscopy (AFM), and
surface recombination velocity (SRV) measurements. Vibrational spectra of ethynyl-
terminated Si(111) surfaces exhibit acetylenic C-H and C≡C stretching modes that are
oriented perpendicular to the surface, while spectra of propynyl-terminated Si(111)
surfaces show a C-H symmetric bending (umbrella) mode also oriented perpendicular to
the surface. LEED patterns indicate the preservation of a 1 × 1 surface unit cell, and
AFM images show the preservation of atomic terraces. Ethynyl-terminated Si(111)
surfaces were deprotonated with a strong base and soaked in CD$_3$OD to produce
partially deuterated ethyne functionality on the surface, demonstrating the reactivity of
the terminal alkyne moiety.

COLL 181

Preparation of anisotropic liquid crystal particles using microfluidics

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The 60 mm sized liquid crystal porous particles were prepared using microfluidics and
UV polymerization with RM257/5CB mixtures and their structures were studied using
micro beam X-ray diffraction. The RM257/5CB droplets coated with SDS and PVA
showed the radical and bipolar configurations, respectively and the UV polymerization
locked their orientation into solid particles. During UV polymerization, the magnetic field
was applied to align the anisotropic bipolar RM257/5CB droplets coated with PVA.
When UV beam direction is parallel to the axis of the two defect poles of the bipolar
droplet, the high anisotropic liquid crystal particles were produced. Without magnetic
field during UV polymerization, the produced LC particles had helical structures due to
replacement of energetically costly splay packing with twisted packing at the defect
poles. The detailed structures of the LC particles were studied with more than 200 two-
dimensional micro-beam X-ray diffraction patterns for one LC particle, for the first time.
The porous structure induced the infiltration of 5CB into LC particles which caused the
rotation of the anisotropic LC particles in the PI-coated LC cell along the rubbing
direction. The combination of the porous structure and alignment of the LC chains in the
anisotropic LC particles exhibited a unique rotating ability in the LC cell.

COLL 182

Preparation and characterization of nylon 6 compounds using the nylon 6-grafted
graphene oxide

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Nylon 6 compounds were prepared using master batch (MB) chips containing nylon 6-grafted graphene oxide (GO$_{\text{graft}}$), which had been prepared using an \textit{in-situ} polymerization method with GO dispersed in a e-caprolactam monomer with 6-aminocaproic acid as the initiator. The MB chips were well compounded with the virgin nylon 6 chips with good processibility. The GO$_{\text{graft}}$ showed good dispersity in m-cresol, formic acid and sulfuric acid compared to the pure reduced GO indicating that the nylon 6 chains were grafted successfully on the GO sheets, which was also confirmed by atomic force microscopy. This GO$_{\text{graft}}$ improved the modulus of the compound by 139 % by incorporating 0.015 wt % of the GO in the polymer matrix but the elongation at break decreased. The increase in modulus by incorporating small amounts of GO might be due to the good dispersity of the GO in the polymer matrix as well as the strong interactions between them.

COLL 183

Solvent-dependent complexation of DNA using small mono-cationic peptides

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In recent years there have been numerous approaches to develop non-viral vehicles for the delivery of nucleic acids that combine high transfection efficiencies with low cytotoxicity. Prominent examples are cationic polymers and liposomes. A major drawback of these materials is the high positive charge density, which is poorly tolerated by cells and tissues [1]. To overcome this limitation, we complexed double-stranded DNA using small mono-cationic peptides containing a hydrophilic and a hydrophobic block of amino acids in their molecular structure. We found that the binding process is initiated by electrostatic interactions and stabilized by hydrophobic contacts between neighboring peptide molecules.

In our experiments, we used a decapeptide to form complexes with short 22 base pair DNA. We obtained nano-sized aggregates in aqueous media by simple mixing the two dissolved components. Agarose gel electrophoresis was used to determine the ability of the peptide to interact with DNA and to investigate the charge ratio necessary for complete binding. The size of the complexes was characterized by dynamic light scattering (DLS) and transmission electron microscope (TEM) imaging.

Due to the amphiphilic nature of the peptide, it showed remarkable behavior in different solvents. In pure water it formed rod-shaped self-aggregates with a diameter of 8 nm and a length of more than 500 nm. By adding small amounts of DMSO, the tendency to form self-aggregates decreased while the affinity for DNA increased. In this manner it was possible to obtain stable nano-sized complexes with only a moderate excess of positive charges and therefore a reduced toxicity. With further experiments we will show, that this formulation can be adapted for plasmid DNA or siRNA delivery.
COLL 184

Adsorption of chromium and arsenic on functionalized magnetic mesoporous silica

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Mesoporous Silica (MCM-41) has shown great potential as an adsorbent owing to the high surface area, tunable pore sizes with narrow distributions and well defined surface properties governed by the surface hydroxyl groups. Surface modification of these particles helps tune the adsorption capacities of the mesoporous silica by providing a more robust surface for the attachment of metal ions in the form of ionic or coordinate complexation. Magnetic mesoporous silica nanoparticles have combined the high adsorption properties of mesoporous silica materials for heavy metals such as As, Cd and Hg, as well as the magnetic properties of the iron oxide which can be used for easy separation. In this study, magnetite (Fe$_3$O$_4$) nanoparticles were coated with MCM-41 and functionalized with (3-Aminopyopyl)triethoxysilane (APTES) and (3-Mercaptopropyl)trimethoxysilane (MPTMS) using a post synthesis grafting method. The parent and the functionalized magnetic silica samples were characterized using powder X-ray diffraction (pXRD), thermal gravimetric analysis (TGA), Fourier Transform Infrared (FTIR) spectroscopy and nitrogen adsorption desorption isotherms for surface area and pore volumes. These materials were evaluated for Cr(III) and As(III) adsorption from aqueous solutions. The APTES-functionalized magnetic mesoporous silica displayed the highest adsorption capacity for Cr(III) of all the materials evaluated in this study. The high Cr(III) adsorption capacity was attributed to a synergistic effect of magnetite nanoparticles and amine functionalization on MCM-41 as well as a judicious choice of pH. The adsorption capacity of these materials for As(III) was not as high as for Cr(III).

COLL 185

Application of silver arrays on gold mirrors to surface enhanced fluorescence

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Silver arrays were prepared on gold mirrors using a mask of polystyrene nanoparticles and a vapor deposition technique. The silver arrays were characterized using AFM, SEM, and confocal microscopy. The silver arrays on gold mirrors were used for surface-enhanced fluorescence studies.
Exploiting nonequilibrium behavior in soft matter for the rational design of advanced materials

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Colloidal particles can stabilize fluid interfaces in a manner similar to amphiphilic surfactants. A key difference however is that particles can become trapped at an interface with adsorption energies orders of magnitude greater than the thermal energy, \( kT \), effectively “locking in” a non-equilibrium configuration of the fluid species. This phenomenon informs a robust bottom-up approach for synthesis of functional materials with higher-order structure using colloidal particles with tunable chemistry and geometry as building blocks. Familiar examples are particle-stabilized (Pickering) emulsions and foams, which are widely utilized in consumer products, oil recovery, foods, and pharmaceuticals. In this research, self-assembly of colloidal particles at fluid interfaces is used to direct the microstructure and functionality of a new class of porous and composite materials based on bicontinuous emulsions. Here, colloidal particles with specific wetting properties kinetically arrest spinodal decomposition of a partially-miscible liquid pair. The resultant non-equilibrium microstructure, known as a bijel, is then used as a general platform to synthesize a novel family of bicontinuous macroporous, hierarchically porous, and composite materials with tunable chemistry and morphology. The assembly of particles at the interface provides a means to percolate their properties in composite structures and generate hierarchical assemblies on widely separated length scales. Post-processing bijels to form functional materials is accomplished using several approaches, including electrodeposition, CVD, nanocasting, dealloying, or combinations thereof. This flexible, scalable, and inexpensive approach allows for the rational design of microstructured materials for diverse applications in catalysis, separations, tissue engineering, and renewable energy systems.

Mechanism of chloride-induced silver nanoparticle aggregation

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Elucidating the mechanism of silver particle aggregation is important in surface enhanced Raman spectroscopy because of the greater enhancement associated with
aggregated particles. Also, aggregation is an important process that has to be considered in environmental and biological systems. It is well known that adding salts to a colloid solution affects the aggregation process, not only because of the increase in ionic strength, but also, at times, because of adsorbate exchange which can affect the nanoparticle surface directly. This is particularly true of chloride ions, and we have focused on studying the effects of this ion by monitoring the size and shape of the surface plasmon resonance (SPR) peak near 400 nm.

We have measured the temperature dependence of the rate of chloride-induced nanoparticle aggregation between 0°C and 40°C, and have found a negative apparent Arrhenius activation energy of about -70 kJ/mol. Although calculations of bimolecular rate constants using DLVO theory can show an inverse temperature dependence, the apparent activation energy is generally small and does not explain the large values that we observe. This indicates that the mechanism is complex with the initial bimolecular association not being the rate-limiting step.

Above 40°C, surface decomposition appears to dominate the rate of decrease of the SPR peak, so we have measured the temperature dependence of the decomposition rate by adding NaCl at lower concentrations where no aggregation takes place. This rate has been found to increase significantly with increasing temperature, and can compete with particle aggregation in reducing the amount of silver found in single nanoparticles.

COLL 188

Supported lipid bilayer removal by buffer flow

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Multiple methods of isolating and purifying membrane proteins are currently in use or under investigation. A family of promising methods uses supported lipid bilayers (SLBs) to provide a native-like environment during the separation process. Many of these processes, such as line electrophoresis and electrophoretic/electroosmotic focusing, produce bands of purified membrane components. While SLB techniques are promising for separations, the solid support inherent in SLB techniques is a challenge for protein characterization, as many membrane processes involve transmembrane signaling or transport. Thus, a method that converts SLBs into lipid vesicles would be valuable. We have shown that a region of lipids may be selectively removed from the solid support by fast buffer flow in a single-channel microfluidic device. The stripping procedure is robust enough that stripping was observed in multiple microfluidic devices. Stripping probably results in the formation of lipid vesicles, and when coupled with SLB membrane protein separation techniques should result in vesicles containing purified membrane protein.
Hollow spherical gold nanoparticle superstructures with size-dependent drug release properties

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Previously, spherical gold nanoparticle superstructures (or gold hollow spheres, GHSs) with varied sizes (MGHSs, 75.3 ± 12.4 nm and LGHSs, 149.7 ± 30.8 nm) were prepared using a peptide–based method and both displayed broad SPR peaks in the NIR window (650-900 nm). In this study, the size-dependent drug release properties of the medium and large GHSs are demonstrated. Specifically, LGHSs can be degraded either using a peptidase enzyme or via laser irradiation at 805nm, while MGHSs can be degraded only via laser irradiation. By using various irradiation times and powers, under the same condition, LGHSs tend to degrade more efficiently than MGHSs. An anti-cancer drug, doxorubicin, was loaded in situ during the synthesis of both MGHSs and LGHSs. Size-dependent drug release properties were studied. Peptidase can cause drug release from LGHSs while laser irradiation induces drug release from both MGHSs and LGHSs.

Polymer-collapsed iron oxide nanoparticles for arsenic uptake
Although relatively scarce, arsenic is ubiquitous and is a major health hazard. For effective uptake of arsenic from water, this study utilized iron-based particles for adsorption and removal, thus allowing for potential development of inexpensive filtration systems. Iron oxide nanoparticles, approximately 10 nm in size, were synthesized using the single polymer chain-collapse method, resulting in a highly versatile active ingredient that can be implemented in various forms. A comparison of such configurations will be presented, including the deployment of nanoparticles as dispersion in arsenic solution or as a nanocomposite. In filtration methods involving dispersed nanoparticles, magnetite particles were removed magnetically while others were removed using salt precipitation. In methods involving nanocomposites, particles were embedded in polyelectrolyte multilayers or as standalone iron oxide-polymer solid. This technology presents a versatile method for the deployment of iron oxide nanoparticles suitable for inexpensive arsenic filtration in various settings.

COLL 191

Synthesis of inverse core shell structures of cadmium sulfide – cadmium selenide

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Quantum dots with cadmium selenide cores and cadmium sulfide shells, called Type I nanocrystals, have previously been synthesized by combining cadmium with sulfur and selenium precursors. (Ruberu, 2012). The core is composed of cadmium selenide due to the higher reactivity of the selenium precursor as compared to the sulfur precursor. Type II nanocrystals could be formed if the reactivity of the selenium precursor was less reactive than the sulfur precursor, causing a core composed of cadmium sulfide and a cadmium selenide shell to form. Tris(pentafluorophenyl) phosphine sulfide and tris(2-methoxyphenyl) phosphine selenide have been identified as potential precursors which would allow for Type II nanocrystal synthesis. Type II nanocrystals could potentially be used as a catalyst to in a sunlight driven process to break down biomass or other catalytic applications as well as in quantum dot sensitized solar cells.

COLL 192

Green synthesis of gold nanoparticles using chondroitin sulfate and their applications for melamine nanosensing

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Chondroitin sulfate, a type of glycosaminoglycan, is a linear polysaccharide which possesses high negative charges in its sulfate and carboxylate groups. Green synthesis of gold nanoparticles (AuNPs) is performed using chondroitin sulfate (CS) by mixing gold salts and CS with heating. No other chemicals are used for the synthetic steps providing a complete green route. The as-prepared AuNPs (CS-AuNPs) are characterized by microscopic and spectroscopic methods. The result from the inductively coupled plasma-atomic emission spectroscopy indicates that the reaction yield is 80.1%. Spherical shaped AuNPs that have an average diameter of 44.7 nm were observed by the atomic force microscopy. Interestingly, the CS chains positioned between the AuNPs play an important role as a stabilizer. Detecting melamine using the CS-AuNPs is a simplified nanosensing method compared to other conventional methods. When the melamine concentration of the AuNP solution increases, the intensity of the UV-visible absorbance at 530 nm decreases. Meanwhile, a new peak appeared at 620 nm, which offers a linear relationship between the absorbance ratio (A620/A530) in the range of 0.1–10 μM of melamine concentration. The melamine spiked in real infant formula is quantified with CS-AuNPs solution at concentrations as low as 12.6 ppb. For a quick on-site screening of melamine in milk products, melamine nanosensing using CS-AuNPs could be a promising technique.

### COLL 193

**Chlorogenic acid-functionalized silver nanoparticles: Green synthesis, characterization, and excellent antibacterial activities against Pseudomonas aeruginosa**

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The functionalization of natural products for the preparation of metallic nanoparticles (NPs) increases the biocompatibility of the resultant NPs. Furthermore, the process is simple, eco-friendly and easy to scale-up. Specifically, chemical reducing agents for the conversion of metal ions to metallic NPs is avoided which further contributes to the current sustainability initiatives. In the current report, chlorogenic acid (CGA, a caffeic acid ester of quinic acid) is selected as a green reducing agent for the functionalization of silver nanoparticles (AgNPs). Silver salts are reduced to AgNPs by CGA without the use of any other chemicals. CGA is a polyphenol compounds that has beneficial effects on human health including chemopreventive, anti-arthritis, anti-oxidant, anti-thrombotic, anti-inflammatory, anti-hypertensive, cholesterol-lowering, and neuroprotective activities. The successful functionalization of CGA on AgNPs (CGA-AgNPs) is confirmed by various spectroscopic and microscopic techniques. The reaction yield is measured to be 95.4% by inductively coupled plasma mass spectrometry. Mostly spherical- and irregular-shaped AgNPs with average diameter 19.29 nm are observed from the microscopic images. The -C=O functional group of CGA is most likely involved in functionalization onto AgNPs. Interestingly, CGA-AgNPs exert a superior antibacterial...
activity against two strains of *Pseudomonas aeruginosa* among 20 strains of Gram-positive and Gram-negative bacteria. For the green synthesis of AgNPs, the current results show that the biologically-active compounds from plants are a potential powerful reducing agent.

**COLL 194**

**Fabrication of bi-metallic nanoparticles loaded onto TiO2 substrates**

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The introduction of noble metals adsorbed on TiO2 substrates can affect the intrinsic catalytic properties of TiO2, however most research has been focused on single species of adsorbed noble metals. The properties of bi-metallic particles loaded onto TiO2 substrates, especially at the nanoscale, have yet to be extensively observed. Our research focuses on the fabrication of distinct noble bi-metallic nanoparticles loaded onto TiO2 particle arrays to closely observe the catalytic activity, chemistry, signal enhancement, and other potential projects that can lead to new observations. Sequential photodeposition of noble metals is accomplished through UV light exposure where metal precursors are reduced and deposited onto TiO2 linear nanoparticles in solution. Distinct Au or Pt nanoparticles have been deposited onto the surface of our TiO2 linear arrays as confirmed by SEM and TEM. Confirmation of metal species has been accomplished by XPS and EDS. Current research has been focused on the development of a method to co-deposit noble metal particles onto the surface of our TiO2 arrays. Our TiO2 arrays have also shown to photo-degrade methylene blue, the introduction of metal species might show progress in degradation. Previous work in our group has proved that polarized Raman spectroscopy performed on Ag nanoparticle arrays yields a significant increase in signal[1]. Similar enhancement may be observed from single or even bi-metallic nanoparticles loaded onto TiO2.
TiO$_2$ particles loaded with platinum nanoparticles. These particles will be examined for their SERS and pollutant degradation ability.

**COLL 195**

**Surface functionalization and passivation of the (111) faces of gallium phosphide for solar energy conversion applications**

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Functionalized benzyl groups and pyridyl groups were reacted onto the gallium-rich (111)A and phosphorus-rich (111)B faces of gallium phosphide (GaP), in the interest of passivating surface recombination sites, probing the chemical states of surface atoms, and adding molecular functionality to the surface for the covalent attachment of catalysts for photoelectrochemical systems, such as pyridine for CO$_2$ conversion to fuels.

The GaP (111)A surface was chlorinated by literature procedures, then functionalized with tris(4-fluorophenyl)phosphine, (P(FC$_6$H$_4$)$_3$. The GaP (111)B was functionalized with either 4-fluorobenzyl bromide, 4-trifluorobenzyl bromide, or 2-(bromomethyl) pyridine hydrobromide.

X-ray photoelectron spectroscopy (XPS) was used to quantify the percentage of surface sites bound to a reagent molecule. The signal intensities of the heteroatom and bulk
substrate peaks were consistent with a phosphine coverage of 10% on the (111)A face. The phosphine appears to have bound to terminal Ga sites as expected while unfunctionalized sites remained chlorine terminated. Similarly, the 4-fluorobenzyl group coverage was 38%, the 4-trifluorobenzyl group coverage was 30%, and the 2-pyridyl group coverage was 59%. Following published work on indium phosphide, the benzyl bromides were expected to bind to the surface via a surface-bound hydroxyl group displacing the bromine. The benzyl groups are bound as expected, but the detection of ionic bromine on the surface calls the proposed mechanism into question. Further studies of surface reactivity would clarify the chemical states of surface atoms before and after the reaction.

Steady-state photoluminescence (PL) measurements show an increase in PL intensity of the functionalized surfaces compared to freshly etched (111) surfaces, indicating partial passivation of electronic trap states corresponding with surface oxide species. This is consistent with XPS spectra of the functionalized surfaces that show less than 1 monolayer of surface oxide coverage.

**COLL 196**

**Polyoxometalates for solution based processing of M$_2$O$_5$ (M = Ta, Nb) thin films**

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Polyoxometalates of tantalum and niobium were studied as potential precursors for the solution based processing of M$_2$O$_5$ thin films, where M = Ta or Nb. The polyoxometalates were characterized in the solid state with Raman and infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray spectroscopy, and X-ray diffraction. The precursor solutions of the same polyoxometalates were characterized via small and wide angle X-ray scattering, and Raman spectroscopy. The precursor solutions were used to deposit thin films of M$_2$O$_5$ by spin coating under ambient conditions. Precursor solution concentration and the annealing temperatures were varied to study the effect on thin film quality, thickness, and density. X-ray reflectivity was used to determine film density, thickness, and roughness. Ellipsometry measurements of film thickness and roughness were compared to reflectivity results. X-ray diffraction was used to verify the phases of the films. The films were imaged using cross sectional scanning electron microscopy.

**COLL 197**

**Nanocrystalline SnO$_2$ thin films prepared by the hydrolysis of tin(IV) isopropoxide and doctor-blade deposition**
A method for the preparation of nanocrystalline SnO$_2$ films is presented. The doctor-blade method is a simple and low cost alternative method to spin- and dip-coating of metal oxide films and has been used previously in the fabrication of TiO$_2$ and ZnO films. In our approach, SnO$_2$ is synthesized from the hydrolysis of tin(IV) isopropoxide. The resulting colloidal suspension is then concentrated by evaporating off water until a thicker glue-like consistency is achieved by eye. The correct consistency is vital to producing quality films which adhere uniformly to the glass substrate surface. To achieve the same consistency when preparing TiO$_2$ films requires the removal of much less water. The SnO$_2$ colloid is heated overnight in an acid digestion vessel at 200°C. Poly ethylene glycol (PEG) is added to the SnO$_2$ as a binder. The doctor blade method involves using a small cylindrical glass object, such as the end of a pasteur pipette, to spread the SnO$_2$ across a substrate creating a uniform film. Nanocrystalline films are achieved with an annealing step at 450 °C. SnO$_2$ films with an average thickness of 2 microns and an average particle size of 25 nm were characterized via scanning electron microscopy. The cassiterite phase of SnO$_2$ was confirmed via X-ray diffraction. Surface chemistry experiments are ongoing, with future work exploring the catalytic nature of these SnO$_2$ films.

**COLL 198**

**Silane stabilized metallic nanoparticles as intermediates for surface modification reactions**

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The transformation via surface modification of nanomaterials in the organic media is a very useful method for the preparation of unique nanocomposites. Such a strategy has been shown to provide highly active, stable, and dispersible metal nanoparticles, because the dispersibility and reactivity play a key role in catalysis, conductivity, and their optical and SERS properties.

In this presentation, a new approach will be presented where silane stabilized metal nanoparticles are redecorated with new ligands in an attempt to tailor the optoelectronic properties of the nanomaterials. We will reveal that the very active silver nanoparticle weakly coordinates to a hydrosilane stabilizing agent, which undergoes stabilizing agent (surfactant) exchange reactions with nitrogen, phosphorus and oxygen containing ligands and even with other functional silans. In addition we will present first example of an exchange reaction on the surface of metallic nanoparticles with octakis-dimethylsiloxy-T8-silsesquioxane (T8) to produce unique multi functional nanocomposites.
Synthesis, characterization, and properties of polyaniline nanofibers using fluorescent TPA-BTD-BN as dopant

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Polyaniline (PANI) nanostructures have received special attention due to its low cost, easy preparation, excellent environmental stability, highly π-conjugated polymeric chains and unique properties which are easily controlled by oxidation and protonation. [1] The preparation of the multi-functionalized conducting polymer nanostructures to match the requirements of various applications in optics, electronics and biology has become the hot topic. Particularly, the unique photoluminescence properties of PANI depend on its redox state have received more and more attention[2-4]. In this paper, PANI nanocomposites with a high conductivity and strong fluorescence doped with a new prepared fluorescein TPA–BTD–BN have been successfully synthesized via a simplified template-free method (STFM) using FeCl₃ as oxidant and dopants. The resulting nanofiber with an average diameter about 60 nm exhibited strong photoluminescence intensity. Room-temperature conductivity of compressed pellets measured as high as 0.45 S·cm⁻¹ indicate highly π-conjugated polymeric chains in conduction system. The fluorescence intensity of synthesized composite improves with the increasing content of TPA–BTD–BN. Moreover, the electrical properties of pressed composite pellets were measured from room temperature about 291K down to 132K and semi-conductive behavior was observed that the conductance follow the exponential temperature dependence of three-dimensional variable-range hopping (VRH) model.

Construction of Pt ultrathin films on Co substrate surface using galvanic replacement

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Because of modern social problems such as an environmental pollution and energy crisis, polymer electrolyte fuel cell (PEFC) has been expected as one of the clean and high power sources. PEFC should require Pt as a cathode catalyst. However,
electrocatalytic activity of Pt is not enough to operate PEFC and moreover, Pt is precious and expensive. Thus, in order to use PEFC generally, electrocatalytic activity of Pt and loading amount of Pt should be increased and decreased, respectively. On the other hand, ultrathin metal layers formed on the different metal substrate often have higher electrocatalytic activity than substrate and deposited metals. In this study, we try to construct Pt ultrathin films on Co substrate surface using galvanic replacement method and structure of the prepared Pt ultrathin films on Co was investigated by angle-resolved X-ray photoelectron spectroscopy (ARXPS). Based on the ARXPS results, we confirmed that Pt ultrathin films formed on the Co surface by galvanic replacement.

COLL 202

Construction and structural analyses of carboxylate terminated self-assembled monolayers on Si(111)

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In order to apply biomolecular functionalities to the modern nanotechnology such as energy conversion and sensors, it is necessary for practical use to extract response against external stimulations as an electrical signal, and is important to introduce biomolecules to semiconductor integrated circuits and to control those sequences. Silicon is one of the most fundamental and important semiconductor materials. Thus, construction of molecular layers on silicon surface may be a step of creating molecular device with a high efficiency. Because self-assembled monolayer (SAM) has high density and high-orientation structure of monolayer, moreover, this is applicable to construct the molecular devices. In this report, two kinds of ester terminated SAMs such as methyl acrylate and ethyl undecylenate SAMs were constructed on Si(111) surface and the properties of these SAMs were investigated by attenuated total reflection - Fourier transformed infrared spectroscopy (ATR-FTIR) and contact angle measurements.

After etching two prisms of n-typed Si(111), methyl acrylate and ethyl undecylenate SAMs were prepared on Si(111) by dipping each Si prism into methyl acrylate and ethyl undecylenate, respectively, and then irradiating UV light (254 nm, 22.0 W) under N2 atmosphere for several hours. After rinsing them with several kinds of solutions, ex situ ATR-FTIR spectra and contact angles with ultrapure water were measured.

Based on the experimental results, we found that the two kinds of SAMs were well-constructed on the Si(111) surface and the ethyl undecylenate SAM had higher density and higher orientation than the methyl acrylate SAM. We also found that C-O single bond of the ethyl undecylenate SAM was oriented more vertical to the Si(111) surface than that of methyl acrylate SAM.
Structural studies on metal-organic frameworks thin films on TiO$_2$(110)

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Metal-organic frameworks (MOFs) are hybrid inorganic-organic solid compounds with high designability of geometry, size, and functionality, and therefore are widely regarded as promising materials for catalysts, separation, gas storage, and molecular recognition. Recently, intensive studies have been reported towards MOFs thin films with liquid phase epitaxy (LPE) to control growth orientation, thickness, and morphology without losing bulk phase properties on oxide substrates, semiconductors, and self-assembled monolayers. However, these challenges have not been extended to an optically transparent semiconductor. For understanding the growth mechanism of MOFs films, X-ray diffraction (XRD) is the most common method, but it requires a few μm-thick generally. In order to overcome this challenge, X-ray absorption fine structure (XAFS), which gives direct structural information with sub-angstrom resolution for polycrystalline and highly disordered material, will be an alternative probe.

In this report, for understanding the growth mechanism of MOFs films, we have examined the structure of HKUST-1 ([Cu$_3$(BTC)$_2$(H$_2$O)$_3$]$_n$ ; BTC = 1,3,5-benzenetricarboxylate) thin films on a single rutile Nb-doped TiO$_2$(110) surface which creates a stable and well-ordered carboxylic molecules monolayer at room temperature. In order to investigate the structure of MOF thin films, polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) technique, XRD and scanning electron microscope (SEM) were performed.

Based on the experimental results of HKUST-1 thin films, we found that HKUST-1 crystallite/nucleus eventually formed on TiO$_2$(110) surface for the ultra thin film. For further growth, XRD and SEM verified that well-oriented HKUST-1 thin films along the $<$111$>$ direction. These results proposed that the adsorption structure of linkers on the surface plays an important role to control the orientation of MOFs films.

Structural studies on first-ordered self-assembly process of flatly adsorbed porphyrin derivatives on Au(111)

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Porphyrrins and metallo-porphyrins are well-known to have unique photochemical and catalytic properties and then have extensively used as a functional molecule in construction of molecular devices. In order to construct molecular devices using porphyrins with higher efficiency, we should control porphyrin ring orientation, namely porphyrin should be flatly adsorbed on the solid substrate surface. Self-assembly (SA) technique is one of the most promising methods to arrange molecule in order on the substrate surface at a molecular level, and then alkylthiol self-assembled monolayers (SAMs) on gold have extensively studied because of their high density, high stability, and high orientation. In this report, a novel porphyrin derivative with 4 thiol groups as surface binding groups to gold and 4 methoxy groups as lateral interaction groups, 5,10,15,20-tetra-(m-mercapto-p-methoxyphenyl) porphyrin (TMP) was newly designed and synthesized, and SA process of TMP on Au(111) single crystal surface was investigated by electrochemical, scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) measurements.

After annealing and quenching of Au(111) disk, TMP SAM on Au(111) was prepared by dipping the Au(111) substrate into benzene solution containing 0.05 mM TMP for certain periods. Linear sweep voltammograms (LSVs) of the Au(111) electrodes modified with TMP SAM, which was prepared for several dipping periods, were measured in 0.1 M KOH solution to estimate density, stability, and orientation. Ex situ STM measurement of TMP SAM on Au(111) was performed in air at room temperature to obtain the molecular arrangement. XPS measurement was carried out to study sulfur state of TMP SAM.

Based on the experimental results, we found that even at initial stage of SA process, TMP was flatly adsorbed at random and that after the phase change, flatly adsorbed TMP was arranged in order on the Au(111) surface at the final stage.

COLL 205

Fabrication of micropatterned molecularly imprinted polymer thin films for detection of atrazine

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In this study, micropatterned molecularly imprinted polymers (MIPs) for recognition of a specific molecule (atrazine) were fabricated on substrates using a micro-contact printing (m-CP) method and photopolymerization. For pattern fabrication, atrazine, methacrylic acid (MAA), and ethylene glycol dimethacrylate (EGDMA) were used as a target molecule, a functional monomer, and a photo-cross-linker, respectively. After placing several droplets of a mixture solution containing all components on the substrate, photopolymerization was performed during a physical contact between the pre-prepared poly(dimethylsiloxane) (PDMS) mold and the substrate. In this process, solvent absorption into the mold and photo-cross-linking simultaneously occurred generating
the micropatterned MICP matrix. The change in sensitivity on the MICP films as atrazine detection sensors were measured using quartz crystal microbalance (QCM) compared to planar MICP films. Furthermore, various specific molecules with similar chemical structures (2,4-dichlorophenoxyacetic acid (2,4-D), ametryn, prometryn) were used to identify improved selectivity on the MICP films.

COLL 206

Directed assembly of colloidal monodisperse polystyrene microspheres induced by alternative current electric field

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Nanomaterials as building blocks offer a promising route for material preparation. And to this purpose, controllable assembly of nanomaterials toward is of great significance. However, the mechanism of the assembling process is still unclear and direct observation of the assembling is difficult for nanomaterials with small size. And therefore, colloidal sub-micro spheres with suitable size will be an ideal platform to study the assembling process and finally control the structures.

Herein, the assembly of colloidal monodisperse polystyrene microspheres under alternative current electric field was applied as a model system. The microspheres of about 1-2 μm in diameter enable us to directly observe the process with common optical microscopes. And the conditions, such as voltage and frequency of the electric field, surface charge of the spheres, solvents and salt concentration, were adjusted to obtain different microstructures of the assembly like chain, island and flower. Preliminary results indicates that surface states of the colloidal spheres plays a key role in the final structures while low dielectric constants of the solvents and high salt concentration only caused agglomeration of the microspheres. This work will bring new insight into the assembling process of the nanomaterials as well as understanding the mechanism controlling the microstructures of the assembly.

COLL 207

Interaction between MNG-3 and carbonate ions at the air/water interface

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Maltose-neopently glycol-3 (MNG-3) at the air-water/aqueous interface and its Langmuir-Schaefer (LS) films were investigated by using surface pressure area isotherm, Brewster angle microscope (BAM), atomic force microscope (AFM) and X-ray reflectivity (XRR). Surface pressure area isotherms show that MNG-3 has different
limiting area according to concentration of carbonate ions in the subphase. BAM images show that more packed and bigger domains are formed at higher pressure and higher concentration of carbonate ions. AFM images also show its close-packed arrangement with higher concentration of carbonate ions and taller height at higher pressure. This different behaviour is originated from ion-dipole intermolecular bonding between hydroxyl groups (maltose part) of MNG-3 and carbonate ions which intrude between MNG-3 molecules.

COLL 208

Correlation between surface and near-surface chemistry of FeS$_2$ and the photoelectrochemistry of FeS$_2$/liquid half-cells

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Pyrite (FeS$_2$) is a naturally abundant and nontoxic material with a suitable bandgap of 0.95 eV and high absorption coefficient. It is a potential candidate for incorporation into solar-energy-conversion devices. FeS$_2$ / I$_3^-$ (aq), I$^-$ (aq) half-cells have displayed near-unity photon-to-electron conversion efficiency but low photovoltages (~ 200 mV). Both computational and experimental results suggest that deleterious surface chemistry has limited the achieved photovoltages. It is not known which chemical surface species limit performance, or how to remove those species and prevent their formation. The photoelectrochemistry of FeS$_2$ / liquid half-cells has been investigated as a function of surface-chemical treatments. This poster presents the correlation between surface treatments (e.g. chemical or thermal), resulting surface chemistry, and photoelectrochemistry.

COLL 209

Biomimetic surface for water harvesting

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Water collection inspired from beetles, cactus, moss, lizards, etc in desert can provide the solutions on water shortage toward sustainable earth and life. The ideas from the nature innovate the function of the materials and improve the efficiency of the system ecofriendly. Here, the surfaces for the water harvesting from the air are reported to enhance the energy efficiency and the collected water volume. The several patterns are fabricated on the metal surface via nano/microfabrication methods for example, wet etching, photolithography, and nanoparticle coating. The fabricated surface is also modified chemically to control the wettability properties; contact angle and sliding angles. The condensation, coalescence, and sliding behavior of the water droplets are observed in micro and macro-scale ranges.
Development of surface chemistry with new model to simulate biosensor kinetic for blood cholesterol detection

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This paper represents the study of developing surface chemistry for amperometric biosensor by using systems of new formulation techniques

Studies of defects in MgO by using NEXAFS and XPS

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Magnesium oxide (MgO) is an important material from a fundamental physical point of view and is widely used in the fields of catalytic, optical and electrical applications. Affecting the materials' characteristics, it is recognized that defects in MgO are important for its applications. One of the important defects in MgO is an oxygen (O) vacancy. In this study, the annealing effect of the O vacancy in MgO induced by hydrogen reduction was studied by using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS).

The MgO powder (~ 50 nm) was, at first, annealed at various temperatures ranging from 373 K to 873 K for 2 hours in hydrogen atmosphere. After the annealing, each powder was slowly cooled. Mg K-edge and O K-edge NEXAFS spectra measurements of the MgO powder were performed at the beamline BL 2A of UVSOR and at the beamline BL 12 of SAGA-LS in Japan, respectively.

In the NEXAFS spectra, in addition to main peaks at around 536 eV in the O K-edge region, two peaks were also observed at the lower photon energy side of the main peaks. The two peaks were not reproduced in theoretical calculation nor observed for bulk MgO, indicating the two peaks are attributed to species on the MgO surface. On the other hand, XPS spectra showed the presence of hydroxide and carbonate on the annealed MgO powder in hydrogen atmosphere. There is a possibility that the assignment of the two peaks is Mg(OH)₂ and/or, MgCO₃ and/or, H₂O and/or, CO₂ and/or, their complex. There molecules were adsorbed on the oxygen defects. The
intensities of these two peaks in the NEXAFS spectra were changed by annealing in hydrogen atmosphere. These results indicate that the oxygen vacancies were induced by hydrogen reduction and the number of vacancies was dependent on the treatment temperature.

COLL 212

Influence of PEGylation degree on the mobility of polycationic nanoparticles

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Despite their wide variety of applications, efficacy of nano-sized drug delivery systems is severely limited by different barriers inside the body. One major obstacle is the extracellular matrix (ECM). Here, small, neutral and hydrophilic nanoparticles are advantageous regarding particle transport [1]. Our aim is to develop a model gene carrier system based on anionic nanoparticles with a coating of branched poly(ethylene imine) (brPEI) which is able to complex nucleic acids [2]. We focus on modifying surface properties of these nanoparticles through a neutral poly(ethylene glycol) (PEG) shielding to improve their mobility in charged matrices.

Anionic silica nanoparticles were coated with one layer of brPEI or fluorescein isothiocyanate (FITC)-labeled brPEI. PEGylation of PEI-coated particles took place in borate buffer using methoxy PEG succinimidyl active esters with different molecular weights. Subsequently, particle characterization was performed by dynamic light scattering (DLS). To estimate the mobility of nanoparticles, fluorescence recovery after photobleaching (FRAP) was conducted in various ECM-like gels.

According to our DLS measurements the size of brPEI-coated particles increased rapidly after the first day of storage, whereby PEGylated particles exhibited steady diameters for at least seven days. Furthermore, lower polydispersity indices were observed for PEGylated samples. Regarding the zeta-potential a decrease from positive to neutral values was measured depending on the degree of PEGylation. In our FRAP experiments we could show that fluorescence recovery was more effective for higher PEGylation degrees.

We proved that the PEG shielding of brPEI-coated particles prevented colloidal instability and aggregation. The surface charge decreased as a function of the amount of bound PEG molecules on the particles. In addition, surface properties were successfully modified to achieve higher particle mobilities in ECM.


COLL 213

Evaluating aggregation kinetics of gold nanoparticles using SERS

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Gold nanoparticles exhibit novel localized surface plasmon resonance (LSPR) which depend on their shape, size, and local dielectric environment and serve as substrates for the detection of small molecules using surface-enhanced Raman scattering (SERS). In this presentation, the time dependent LSPR spectral changes of solution-phase gold nanoparticles upon addition of small molecules are used to estimate the size of both primary and clustered nanoparticles. Impacts of primary nanoparticle concentration and size as well as molecular concentration reveal interesting size and time dependent trends. Next, evaluation of these data using reaction and diffusion-limited aggregation models suggests that all parameters (nanoparticle size, nanoparticle concentration, and molecular concentration) are relevant in understanding the time-dependent LSPR and SERS spectral results. By relating the change of these spectroscopic signals to changes in nanoparticle cluster size, the kinetics of nanoparticle agglomeration and aggregation can be better understood and accounted for in future applications in biological and chemical sensing.

COLL 214

In vitro characterization of cell viability on nanolatex multilayers films

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Natural Rubber latex (NRL) is a colloidal complex with particles sizes varying from 5 to 5000 nm. Casting membranes produced using NRL can accelerate cells proliferation and induce revascularization1, similar when in multilayer films configuration.2 But to achieve organized multilayer films3 of NRL the particles sizes distribution should be reduced and controlled. A Nanolatex solution, with particles below 200 nm, was obtained performing a series of centrifugations and filtration on NRL. Multilayer films of nanolatex were then mounted with polyethylenimine (PEI) and polyallylamine hydrochloride (PAH) up to 10 layer pairs. The increase of the films thickness per deposited layer was detected by ellipsometry (PlasMos GmbH) using 632.8 nm laser beam focusing on the sample at a fixed angle of 45 degrees. PEI/Nano was thicker than PAH/Nano, which also reflected on the contact angles and roughness of both surfaces. Films of PEI/Nano presented angles of 82º and roughness of 3.3 nm, while PAH/Nano showed angles of 69º and roughness of 0.7 nm. Apparently, those surfaces different characteristics had some impact on the 3T3 cells reactions. Films of (PEI/Nano)5 and (PAH/Nano)5 on round glass slides were directly seeded with 10^3 3T3 cells and kept in
culture conditions for 1, 3 and 7 days [DEMEM medium with 10% BCS and antibiotics at 37ºC in 5% CO2]. On each culture day the cells were count by MTT assay, and photos were taken for morphological analysis. Casting of nanolatex was also analyzed and polystyrene culture well was used as control. On nanolatex casting the amount of cells were higher than control up to 3 days, but on \((\text{PAH/Nano})_5\) it was extended to 7 days. The multilayer configuration might have preserved the bioactivity for longer time. However, \((\text{PEI/Nano})_5\) showed for 1 day a double amount of cells than control, but it got decreased on the following days. We assume those results were influenced not only by chemicals difference (PEI and PAH) but also by the surface characteristics.


**COLL 215**

**Effects of peptide aggregation on the biomimetic precipitation of titania**

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Titanium dioxide (titania) is a common material that has found uses in basic commodities such as sunblock and for food preservation. Environmentally-friendly (green) techniques for the precipitation of titania would eliminate the need for harsh chemical conditions traditionally used. Efforts are desired that explore biomimetic, peptide-aided syntheses to affect controlled titania precipitation with consistent morphologies.

A set of ten peptides (< 12mer) containing lysine (K) and serine (S) residues have been investigated to study the morphological control on titania precipitation at room temperature. Various morphologies have been obtained, and SEM studies will be presented discussing structures achieved. Titania structures are highly dependent on precipitation conditions. For example, precipitation studies (pH 7.2, 25 mM Tris HCl buffer) with the smallest peptide, KSSKK, results in particles with nanospherical structures. Assay data discussing quantification of titania precipitated and Dynamic Light Scattering (DLS) studies will also be discussed. These small SK peptides are highly charged species and do aggregate but display limited structural organization on
their own in aqueous solution. DLS studies will aim to address the effects of peptide aggregation on titania particle sizes.

COLL 216

Nanostructures based SERS sensors for detection of chemicals

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Surface-enhanced Raman spectroscopy (SERS) based nanostructured sensors were fabricated for sensitive detection of chemicals. Silicon nanospikes were first photo-inscribed on silicon wafers with femto-second laser pulses at 400 nm. Silver nanoparticles were then formed on the nanostructures by reducing silver nitrate with hydrazine and Vitamin C for plasmonic enhancement. The fabricated SERS sensors were able to detect Rhodamine 6G molecules at $10^{-12}$ M in water, indicating that the sensor is capable of detecting about 12 molecules in the focal spot of the excitation laser beam. An enhancement of $10^7$ was estimated. Experimental details and characterization will be presented.
In situ generated surface-bound palladium-gold bimetallic nanoparticles and their potential towards electrochemical methanol oxidation

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Metallic and bimetallic nanoparticles are becoming increasingly important due to their catalytic applications. The formation of two dimensional nanoparticle assemblies that do not aggregate on various functionalized surfaces is of considerable interest. The present ongoing research involves the formation of palladium-gold (Pd-Au) bimetallic nanoparticle assemblies directly on silicon and indium tin oxide (ITO) coated glass surfaces. Varying ratios of gold and palladium are used to generate nine unique combinations ranging from only palladium to only gold. Atomic Force Microscopy (AFM) is used to characterize the structure of the nanoparticles and surface zeta potential measurement is used to follow the change in surface-charge during different step of the synthetic process. The catalytic applications of each catalyst toward methanol oxidation are observed electrochemically using cyclic voltammetry. Ultraviolet-visible (UV-Vis) spectroscopy is used to observe the optical properties of the bimetallic nanoparticles, giving insight on their alloy or core-shell structure. The catalytic activities of these Pd-Au bimetallic nanoparticle assemblies are assessed for methanol oxidation reaction. As part of our ongoing research, the catalytic activities of these Pd-Au based nanoparticle assemblies will be compared with our previous studies related to palladium and gold nanoparticle assemblies. In addition, palladium-gold bimetallic nanoparticle assemblies generated on ITO surface are also used as catalyst for reduction of 4-nitrophenol into 4-aminophenol in presence of excess sodium borohydride. The course of the reaction is followed by UV-Visible response to calculate the apparent rate constant of the reaction with varying composition of palladium-gold bimetallic nanoparticles.

Compressive sensing sum-frequency-generation microscopy real-time monitoring copper oxidation

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Sum frequency generation imaging with spectroscopic vibrational contrast is a label-free solution for visualizing, identifying, and quantifying a wide range of chemical properties of metal Surfaces. In the practical applications, the fast imaging capabilities is always comprised with the loss of spectroscopic information over a broad spectral bandwidth. Compressive sampling is a new method to capture and represent compressible signals at a rate significantly below the Nyquist rate; the signal is then reconstructed from these projections using an optimization process. Our novel technique has combined the
Compressivesampling theory with Sum frequency generation imaging to address the current technique challenges in real time chemical diagnostics capabilities. We have applied this novel technique to real time monitor the formation of a thin oxide film on both octadecanethiol (ODT) deposited copper and chemically stripped copper surface. The spontaneous atmospheric oxidation of Cu from an initial reduced state was observed as a change in the non-resonant phase response of the sum frequency generation (SFG) spectral line shape obtained. Over the exposure time, these different regions were observed to gradually undergo Cu oxidation. This finding has a significant contribution toward recognizing that metal surface protection and corrosion.

**COLL 219**

**Cross-linked carbon nanotubes with alkoxy silyl moieties**

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Currently, carbon nanotube research is one of the most active areas of nanoscience because they display a high degree of strength and flexibility, large aspect ratio, low mass density, extraordinary electrical, optical and thermal properties. Because of the substantial van der Waals attraction between CNTs, dispersion of CNTs in solvents or polymeric matrix is hindered; hence CNTs show poor solubility and processibility. CNT surface functionalization aims to modify the surface of the CNTs, which, in turn, dramatically enhances their processibility.

The objective of this research is to convert hydroxyl functionalized multi-walled and single walled carbon nanotubes to siloxy functional nanoconjugates via the hydrolytic condensation of silylmethoxy group with the hydroxyl group attached on the nanotubes. Such a direct substitution of hydroxyl functionalized multiwalled carbon nanotubes (MWCNT-OH) provides an opportunity to create a covalent MWCNT-silica gel network. We will present the results demonstrating CNT functionalization with bifunctional silanes such as bis(trimethoxysilylpropyl)amine which coat around the nanotube and polymerize with other both coated and uncoated tubes. Analysis of these materials was accomplished by using FT-IR, NMR, SEM, TEM, and thermo graphic analysis. Materials produced through this method maintained their amino functionalities which may further be used to complex metals within or onto carbon nanotubes. Polymerized nanotube composites through this method could be tailored to incorporate a wide array of materials such as drugs and recoverable catalysts.

**COLL 220**

**Investigation and identification of electrochemical behavior of high density nanoporous membranes prepared from thin films of supramolecular block copolymer assemblies**
The objective of this work is to investigate electrochemical behavior of thin nanoporous membranes deposited on gold electrodes by means of cyclic voltammetry (CVA). The membranes are prepared using supramolecular block copolymer assemblies (SMA). SMAs are hybrid materials characterized by the ability of one block to selectively interact with a low molecular additive. A main feature of SMAs is the ability to form well-ordered arrays of nanoscopic pores upon selective extraction of the additive. In order to understand the role of nanoscopic confinement and pore interior upon occurring RedOx processes, we systematically investigate SMA morphology by varying film thicknesses. Morphology and orientation studies are investigated by Atomic Force Microscopy (AFM). We observe strong variations in CVA behavior of the electrochemical label depending on film morphology.

The subject of investigation is an extensively studied SMA composed of poly(styrene-block-4-vinylpyridine) (PS-PVP) which is bound via selective hydrogen bonding of the PVP block with 2-(4'-hydroxybenzeneazo) benzoic acid additive (HABA). The microphase separation of SMA results in well-ordered arrays of domains of PVP+HABA while PS forms the matrix on the working electrode. The periodicity of the SMA domains is of about 28 nm. Extraction of HABA from the domains leaves pores with the diameter of 12 nm. The effect of nanoscopic porosity and pore depth on the electrochemical behavior of the system is evaluated through CVA measurements. Such measurements are performed using hexacyanoferrate complex as the RedOx label. The oxidation and reduction peaks of the label identified using CVA show strong variation depending on the preparation conditions of the SMA membrane.

A deep understanding of the electrochemical processes in nanoscopic membranes will open a venue to cost effective fabrication of nanoscopic features with a variety of shapes, sizes, and density for industrial applications, such as, smart optics, optoelectronics, solar cells, antireflection coatings, etc.

**COLL 221**

**Controlled water and oil penetration of organically modified clays by choice of cationic surfactants with variety of substituents**

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The proposed research work provides recent advances in hydrophobic clay research. The key research opportunities and challenges in the development of structural and
functional hydrophilic nanoclay are addressed in the context of traditional clays. The state of knowledge in processing, characterization, and analysis of nanoclay is presented with a particular emphasis on identifying fundamental structure/property relationships. Cation exchangeable montmorillonite (MMT) rich bentonite clay reacted with surface active quaternary ammonium salts (QAS) with various substituents at the quaternary ammonium moiety having varying chain length for aliphatic hydrocarbons as well as aromatic hydrocarbons and multi branching in aliphatic hydrocarbons. Organically modified clays were characterized by Fourier Transform Infrared Spectroscopy (FTIR), powder X-ray Diffraction Analysis (PXRD), Particle Size Distribution (PSD), Water and oil penetration measurement, Surface area Measurement (BET), Zeta potential and thermo gravimetric analysis (TGA). The loading of the (QAC) detected by C, H, N analysis. The synthesized clays display substituent dependent water and oil penetration. Due to the varying spatial arrangement of each surfactant in the basal planes of clays and the varying nature of stearic hindrance caused by the substituents on Quaternary Ammonium Salts (QAS) alter the Hydrophobicity and oil penetration. The present study throws a light on simple route to control the water and oil penetration of Montmorillonite clays which may be useful for designing clay-composite materials and provides selectivity of solvents for water and oil penetrations.

COLL 222

Soft-solution processing of pristine and doped LaFeO$_3$ microcrystalline powders for applications in energy storage

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Perovskites, such as rare earth ortho-ferrites (RFeO$_3$) present a wide range of technological applications, including oxygen sensors, ceramic membranes for conversion of various hydrocarbons, cathode material for fuel cells and catalysts for hydrocarbon oxidation or hydrogenation. LaFeO$_3$ and its calcium substituted La$_{1-x}$Ca$_x$FeO$_{3-\delta}$ derivatives are structurally robust materials exhibiting a good oxygen diffusivity. This being suitable for the design of electrodes in environmentally-friendly energy storage applications because they are Li free and allow for the oxygen ions to be extracted/inserted topotactically via redox reactions. Along with improved oxygen diffusivity, a battery material should possess a high porosity in order to facilitate the extraction/insertion of cations.

In this work, we report on the rational design of microporous LaFeO$_3$ and La$_{1-x}$Ca$_x$FeO$_{3-\delta}$ micropowders for use in the design of electrodes for Li-free batteries. The morphology, phase purity, chemical composition and specific area of the resulting powders were characterized by a variety of techniques including microscopy, X-ray and electron diffraction, spectroscopy, surface area and thermal analysis. Preliminary results indicated that single phase materials can be obtained by varying the annealing temperature, whereas the pore size can be controlled by adjusting the heating rate during the post-synthesis annealing process. In the next step of this work the powders
are to be incorporated into electrodes and their electrochemical characterization will be performed.

**COLL 223**

**Fluorescence from biomimetic silica nanoparticles**

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Fluorescent silica nanoparticles have the potential to offer a safe, bright, and more stable marker for biological materials. Typical syntheses rely on modified Stober processes to develop these particles. One of the few alternative methods for synthesis of non-fluorescent silica nanoparticles utilizes biomimetic methods, specifically mimicking the methods used by diatoms, a type of unicellular algae, which are known for their ability to create elaborate silica structures. We have recently extended this method to successfully incorporate fluorescent dyes into the synthesis of silica nanoparticles, which has been found to not only be more efficient at dye incorporation, but rapid. This method utilizes the pendant primary amine groups on a polyamine, whereby fluorescent dyes, can easily be attached. These tagged-polyamines can then be reacted with silicic acid to generate fluorescent silica nanoparticles in a single step. Furthermore, the dyes are strongly attached and we have seen that they do not leach out over time, exhibiting long-lived stability. These fluorescent particles have been studied via detailed fluorescence spectroscopy methods, including steady state and time-dependent spectroscopies. The incorporated dye concentration has been optimized to prevent self-quenching, and the quantum yield and fluorescence lifetime measurements demonstrate an enhancement of light emission, with an accompanying increase in brightness. They are also significantly more photostable than the free dyes, as protection within a silica core and rigidification increases the radiative decay rate. We have also quantified the fluorescence of these silica nanoparticles with other dyes, including rhodamine, demonstrating this technique as versatile. As this method can be extended to a variety of fluorescent molecules, colors and wavelengths currently used in the medical field for imaging can be preserved, and this may offer a new, bright, system for standard detections.

**COLL 224**

**Synthesis of composite nanoparticles for optical nanocoding applications**

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Current work in the field of luminescent, semiconductor nanoparticles often combines luminescent nanomaterials with different band gap energies to form core-shell structures (e.g. CdSe/CdS, CdTe/CdSe). This prevents leakage of excited electrons to
non-emitting surface defects and results in an emission quantum yield comparable to the brightest molecular fluorophores like fluorescein. These luminescent core-shell nanomaterials exhibit broad absorbance spectra, narrow emission peaks, high photostability, and size-dependent emission wavelength tunability, which make them attractive alternatives to molecular fluorophores in fluorescence imaging applications. Interestingly, the combinations of CdSe and CdS or CdTe and CdSe in core-shell nanostructures result in a single emission peak, even though these materials emit light at different wavelengths when crystalized separately. Electronic interactions between the core and shell materials is one possible explanation for this phenomenon; however, these interactions are not fully understood. Understanding and controlling these interactions will open possibilities for new composite nanomaterials with unique and useful properties. In this study we aim to form composite core-shell structures with two emitting nanomaterials, CdSe and CdS. The CdSe and CdS luminescent layers are separated by a higher band gap energy material to prevent leakage of electrons from the CdSe core to CdS shell. The study compares the emission properties of CdSe/CdS/ZnS and CdSe/ZnS/CdS/ZnS composite nanostructures. Our experiments aim to optimize the synthesis conditions necessary to separate the emission peaks of CdSe and CdS and to control the ratio between the distinct emission peaks to enable optical coding. The presentation will describe the synthesis of the composite nanomaterials, characterization of their size, morphology and stability using high-resolution transmission electron microscopy (TEM), and light-scattering measurements and their luminescence properties using steady-state luminescence and fluorescent lifetime imaging spectroscopy. These nanocomposites are prime candidates for multiplexed, live cell imaging and labeling assays.

COLL 225

Ferrocene probe investigations of the sphere to rod phase transition for cationic gemini surfactants

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Ionic gemini surfactants are known to adopt various aggregation morphologies that depend on the structure of the surfactant, the surfactant concentration, and the structure and concentration of counterions. We are studying the transition from spherical to rodlike micelles of the cationic gemini surfactant trimethylene 1,3 bis (dodecyldimethylammonium) dibromide (12-3-12), which is sensitive to added counterions, and the similar surfactant tetramethylene 1,4 bis (dodecyldimethylammonium) dibromide (12-4-12), which is rather insensitive to the added counterions so it serves as a control. Previously, viscosity measurements inferred a sphere to rodlike phase transition with the addition of p-fluorobenzoate to 20 mM of 12-3-12, and now we seek to further describe and quantify this transition. To determine morphology and aggregate size, we measure the diffusion of the aggregates using ferrocene as an electrochemically active and NMR active probe. Due to its
hydrophobic nature, ferrocene resides in the micelles, allowing diffusion of the aggregates to be determined with both electrochemistry and pulsed-field-gradient NMR.

**COLL 226**

**Fluorescence study probing the conformational change of protein adsorbed on the nanocolloidal surface**

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By utilizing of enhanced Thioflavin–T (ThT) fluorescence upon binding proteins, we investigate the spectra in an attempt to correlate conformational change (folded or unfolded) over the nanocolloidal surface under various concentrations as well as pHs. The fluorescence intensity was found to increase as concentration of amyloid beta or ovalbumin was increased. Our results provided an evidence of an enhancement of fluorescence prominently in pH 9-pH10. When we tested for a reversibility in observed fluorescence with respect to an external pH fluctuations between pH 4 and pH10, there was a slight sign of reversibility only when 20 nm gold colloid was present. We conclude that fluorescence data can potentially be utilized to correlate the protein conformation over the gold nanocolloidal surface.

**COLL 227**

**Synthesis and characterization of silicon nanoparticles with tunable emission properties**

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Nanotechnology is a rapidly maturing field providing biosensors as well as chemo therapeutic systems. Valuable contributions to this field will come in ways to make these materials less toxic (both biologically and environmentally), more affordable, and with simplified protocols. The use of silicon to form nanoparticles addresses each of these points. We will present the synthesis of silicon nanoparticles in aqueous media utilizing microwave technology. Our focus is to overcome issues concerning competing emission pathways from the silicon core and emission from surface defects that result from oxidized surface states. These surface defects lead to emission in the blue range of the visible spectrum regardless of the size of the particle. In order to provide valuable biocompatible fluorescent materials, the size-tunable core emission must dominate. The presentation will describe a protocol optimizing the synthesis in terms of pH, solvent, temperature and reactants. In addition, we will examine the effects of surface modification with macromolecules in order to enhance chemical and photophysical characteristics such as stability, aggregation prevention, aqueous solubility and
excitation-emission capabilities. We will extensively characterize the nanoparticles utilizing UV-VIS, fluorescence (both steady-state and lifetime measurements), fluorescence quantum yield, DLS, TEM and FT-IR. Particularly, we will describe conditions that provide particle populations of narrow size distribution, high fluorescence yield, and size tunable fluorescent emission.

**COLL 228**

Poly (N-isopropylacrylamide) conjugated monodispersed fluorescent detonation nanodiamond for controllable temozolomide delivery

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Nanodiamond with low cytotoxicity is known as novel material which can pass through the blood brain barrier to provide treatments for many central nervous system disorders in recent years. Meanwhile, polymer is popular for controllable drug release design due to its stimuli responsive behavior with low critical solution temperature (LCST) 32°C. In this study, a sulfur functionalized DND is conjugated with Poly (N-isopropylacrylamide) (PNIPAM) to use as a drug carrier for the first time. Briefly, low temperature annealing is used to create surface defects on DND (SDND) to make it fluorescent and more hydrophilic. Furthermore, PNIPAM is functionalized SDND through a 'grafting from' method: PNIPAM is anchored onto SDND during the free radical polymerization process. This SDND/PNIPAM is used to deliver a FDA approved brain cancer drug—Temozolomide (TMZ) in vitro. TMZ is the only agent which changed clinical practice for GBM to prolong survival of patients. Its main effect is methylation of tumoral DNA to activate the apoptotic pathways causing tumor cell death. In the drug delivery, once the temperature of SDND/PNIPAM is above LCST, the particle will collapse and the hydrophilic TMZ will release. The releasing of TMZ carried by SDND/PNIPAM is carefully studied.

**COLL 229**

Stimulus-responsive nanoparticles stabilized by non-DLVO interactions: Implications of ionic strength and copolymer (x:y) fraction on aggregation kinetics

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Functionalized nanoparticles can assist in stabilizing fluid-fluid interfaces, however, developing and applying the appropriate surface modification presents a challenge because successful application of these nanomaterials for biotechnological, food
processing, and environmental applications requires their long-term stability in elevated ionic strength media. In this respect, surface modification of nanoparticles with responsive polymers offers the opportunity to tune particle interactions thus allowing control of directed self-assembly through changes in stimuli.

Here, we investigate the role of hydrophobicity and physicochemical behavior in suspension on the colloidal stability of responsive core shell nanoparticles based on random copolymers of di(ethylene glycol) methyl ether methacrylate (x=MeO₂MA) and oligo(ethylene glycol) methyl ether methacrylate (y=OEGMA). The nanoparticles Au@(MeO₂MAₙ-co-OEGMAₙ) display tunable, reversible aggregation that is highly dependent on the (x:y) ratio and ionic strength. Effects of these parameters on the initial rate constant of aggregation (k₁₁) are studied using time resolved dynamic light scattering (TR-DLS) experiments. Our findings indicate that different copolymer compositions induce varying degrees of stabilization, characterized by different critical NaCl coagulation concentrations (CCC), although with similar salt sensitivities. Over less than 300 mM increase in NaCl concentration, we observe a two-order of magnitude increase in aggregation rate constants, 4.2x10⁻²⁰<k₁₁<1.8x10⁻¹⁸ m³s⁻¹.

Analysis of the experimental data with an extended Derjaguin-Landau-Verwey-Overbeek (xDLVO) theory that accounts for hydration and osmotic forces is used to explain the stability of these systems. The good agreement between the theory and the experiments suggests that the colloidal stability of Au@(MeO₂MAₙ-co-OEGMAₙ) NPs is regulated by the effective pressure, P₉, arising from the difference between water hydration and salt osmosis. We find the hydration pressure, 2.4<P₉<7.2MPa, scales linearly both with the osmotic pressure and the OEGMA monomer concentration (5<y<20%). Specific knowledge of P₉(y, CₙaCl) enables design of both aggregation kinetics and stability as a function of the co-polymer ratio and stimulus fields.

Synergistic effect of two paramagnetic metals in a single nanocolloid for enhanced magnetic resonance imaging

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Detection of thrombus within fissures of vulnerable atherosclerotic plaques requires a sensitive yet safer contrast agent for magnetic resonance imaging. The recent discovery of nephrogenic systemic fibrosis (NSF) has raised concern over the use of currently approved gadolinium based contrast agents in patients with renal/kidney diseases and created a high, translational barrier for new agents to address.
With this aim in our mind, we explore for the first time dual paramagnetic metal manganese (Mn) and copper (Cu) for a consolidated and synchronous effect from these metals. The goal of this study was to develop a sensitive 'hybrid' Mn-Cu-based molecular imaging agents with high avidity for fibrin.

“Soft” type nano colloids were designed and synthesized as vascularly-constrained \(D_{av}=200 \text{ nm, } z=-23 \text{mV}\) nanoparticles with a core entrapped manganese oleate and a shell presenting copper (II)-DTPA. Organically soluble Mn (II) oleate was suspended in polysorbate and encapsulated by phospholipid mixture to incorporate nominally 100,000 Mn/particle and 20,000 Cu(II)-DTPA per particle. For in vitro targeting, ligand biotin was used as a component of the lipid surfactant. A single slice inversion recovery sequence was used to calculate the particulate (per particle) relaxivities of serially diluted nanoparticles. Fibrin clots supported on silk suture suspended in PBS were targeted with biotinylated NanoCool or control nanocolloids to the fibrin clots with avidin-biotin interactions and fibrin-specific antibodies (NIB5F3). MR images (3T) of the clots were acquired using T1-weighted gradient echo images. MR imaging of targeted and non-targeted particles to fibrin clot phantoms showed clear contrast enhancement, while control clots (non-targeted and targeted without metals) had no (or negligible, \(p<0.05\)) contrast changes. Fibrin-specific hybrid Mn-Cu nanoparticles offer high relaxivity, non-gadolinium imaging agents for sensitive noninvasive MRI of human thrombus.

**COLL 231**

**Multi-photon excited fluorescence near-field scanning optical microscopy with monolayer protected \(\text{Au}_{25}\) nanoclusters reaches super-resolution**

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New approaches in optical imaging techniques are greatly desired to obtain point resolutions reaching nanometric dimensions. Predominantly the realm of electron microscopy, the intricate information such optical imaging techniques could elicit (of the molecular dipoles) are immense. Despite the promise of multi-photon excited fluorescence (mPEF) near-field scanning optical microscopy (NSOM), aperture-based mPEF NSOM was unable to obtain point resolutions below \(~175 \text{ nm}\) using organic chromophores. This difficulty can be partly attributed to the low photo-stability and relatively low two-photon absorption cross sections of the fluorophores. \(\text{Au}_{25}\) nanoclusters have shown unusually large two-photon absorption cross sections \((4.27 \times 10^5 \text{ GM})\) in the solution phase suggesting their potential future applications in super-resolution imaging and sensing.
With the use of single Au$_{25}$ nanoclusters as strong two-photon absorbers we report the observation of two-photon excited fluorescence (2PEF) NSOM resulting in a point resolution of 37 nm ($<\lambda/21$). Interestingly, a ~3-fold enhancement ($1.31 \times 10^6$ GM) of the two-photon absorption cross section in solid is observed for these single nanoclusters. We attribute this enhancement to a local field enhancement effect. According our knowledge this is the first time that aperture-based 2PEF NSOM has been able to obtain point resolutions below 100 nm. Therefore, this study introduces gold nanoclusters as a fluorophore that can be utilized both in multiphoton imaging and that can potentially be used to study spectroscopy at molecular-scale dimensions using super-resolution imaging techniques.

**COLL 232**

**Establishing a direct connection between the Young's modulus and polarizability of millimeter and nanometer-sized organic cocrystals**

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Establishing reliable structure-property relationship of materials is essential for the potential design of novel materials with tunable mechanical, electronic, optical and chemical properties. Current study involves the mechanical characterization of a series of multi-component solids (cocrystals), involving 4,6-di-halo-resocinol, as the template (halo=Cl, Br and I) and trans-1,2-bis(4-pyridyl)ethylene (4,4′-bpe), using Atomic force microscopy (AFM) based nanoindentation technique. AFM uniquely offers spatially resolved (~nm scale) force measurements with pN sensitivity. Herein, force versus
distance measurements on individual nanometer- and millimeter-sized cocrystals were used to determine the Young's moduli. A steady decrease in the Young's modulus was observed with increasing size of the side chain halogen group (from Cl to Br to I), which is attributed to the differences in polarizability and strength of intermolecular interactions between systems. Highly polarizable atoms/groups can facilitate dislocation motion in cocrystals and result in a decrease in stiffness. Further, thermal stability of cocrystals was investigated and a consistent decrease in melting point was observed with increasing size of the side chain halogen group, suggesting further evidence for weaker interactions present with increasing polarizability of cocrystals. Overall, trends obtained herein open a new door to investigate the structure–property relationship of multicomponent systems by establishing a reliable relationship between chemical properties such as polarizability and mechanical properties of materials.

**COLL 233**

**Thermal reduction method to improve the photoluminescence of carbon dots**

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Carbon dots (CDs) have received great attention due to excellent properties such as unique tunable optical property and biocompatibility. In this paper, blue luminescent CDs were prepared by thermal reduction CDs from citric acid. After thermal reduction, the increase of sp² domains in t-CDs and decrease of carboxyl group on the surface of t-CDs enhance the quantum yield of t-CDs which is five folds of CDs. This work may provide a “neat” and eco-friendly pathway to increase the QY of CDs.

**COLL 234**

**NiO/TiO2 bilayer films for photocatalytic degradation of Acid Orange 7 in the absence of light**

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Photocatalysis efficiency of the concept of reductive and oxidative energy storage was investigated. When TiO₂ is subject to UV illumination, electrons from the valence band are transferred to the conduction band. That, in turn, induces electron transfer from the p-type semiconductor to the conduction band of TiO₂. The hole of the p-type semiconductor is not stable, and intercalation from an electrolyte is needed. However, all energy storage photocatalysts that have been developed so far are the reductive energy storage type. In addition, the combination of the oxidative energy storage type with the reductive type would achieve effective storage and usage of solar energy. However, TiO₂ is an n-type semiconductor, from which electrons in its conduction band
are transferred, whereas the holes in its valence band are transferred in a lower extent, so that storage of the oxidative energy of TiO$_2$ is expected to be challenging. Hence, the purpose of this work was to investigate the possibility of using energy stored in NiO/TiO$_2$ bilayer films to activate the photocatalytic reaction in the absence of light. The catalyst was tested for its photocatalytic activity in the degradation of acid orange 7.

**COLL 235**

**Synthesis of gold nanoshell with less than 100 nm diameter and palladium nanoshell on silica core using in situ generated metal nanoparticle seeds**

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Palladium shell of $\sim 11$ to 15 nm thickness has been synthesized successfully by reduction of surface bound palladium ions onto $\sim 200$ nm diameter silica core. The method for generating such nanoshells is based on seed-mediated growth technique. Palladium ions from complex palladium salt are adsorbed onto aminosilane functionalized silica core and subsequently reduce to create *in situ* palladium nanoparticle seeds. These nanoparticle seeds act as the nucleation sites to promote further growth of final palladium overlayer. Palladium nanoparticle seeds generated onto the functionalized silica surface are $\sim 3$ nm in diameter and are uniformly distributed throughout the core surface as observed by transmission electron microscopy (TEM). The thickness of the final palladium shell can be tailored by varying the concentration of the seeded core during the shell formation step. This present method reports the first time synthesis of palladium nanoshell from surface bound palladium nanoparticles seeds compare to earlier reports that use gold nanoparticles as seed to generate final palladium shell. In addition to palladium nanoshells, the current study involves synthesis of gold nanoshells on silica cores that are less than 100 nm diameter using the same method of making palladium nanoshells. Previous work has shown the successful synthesis of gold nanoshell on a 200 nm silica core using the present seed mediated synthesis procedure. Gold nanoshells with a smaller core may find increased application in photo-thermal therapeutic studies.

**COLL 236**

**Nanometer scale localization of semiconductive materials using DNA nanostructures**

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Nanoscale electronic device applications will require the arrangement of materials such as carbon nanotubes (CNT) and metal particles into networks, with precise control of the placement, orientation and spacing being essential. The scaffolded DNA
nanostructures called DNA Origami (DO) can provide a flexible platform for performing supramolecular chemistry, generating complex architectures through the use of simple modifications. Structures have been formed which accommodate various biologically relevant molecules, metal nanoparticles, quantum dots and carbon nanotubes. Origami can themselves be assembled into larger structures extending their potential for small-scale device applications. While the size of current origami constructs is large enough to connect bottom-up methods of patterning with top-down approaches, even larger scale structures can be anticipated which will enable manufacturing breakthroughs, particularly if coupled with indexed localization within arrays. In this presentation approaches to the immobilization of semiconductive materials such as CNTs and quantum dots (QDts) on origami constructs at ∼100 nm spacing, with programmed orientation on both single origami and on multiple micron long linear origami arrays, are reported.

Figure 1: AFM images of a) single rectangular origami (srDO); b) d) one dimensional rectangular origami (1DrDO) c) one dimensional cross-like origami (1DcDO); d) CNTs aligned at the edge of srDO; e) two CNTs aligned on 1DcDO and f) QDot labeled 1DrDO.

Two different lengths of ssDNA wrapped SWCNT, short (∼92 nm±24) and long (∼92 nm±24) nanotubes were bound to the ssDNA rich edges of DO. Figure 1d demonstrates that the nanotubes prefer to localize at the ssDNA rich edges of DO. Furthermore, to localize long CNT’s, multiple origami constructs were assembled into extended one-dimensional DO arrays. This array has been used to successfully align pairs of CNTs exceeding ∼500 nm in length in a parallel orientation (Fig. 1e). To demonstrate the
concept of using multiple micron long origami substrates to organize multiple QDts into arrays, we reacted QDts and ∼5 micron 1DrDO. The AFM image in Fig. 1f shows part of a DO array used to localize multiple QDts with ∼44±3 nm spacing and ∼96±3 nm pitch. These results, readily bridging the nanometer to micron size domains, indicate a promising future path toward the development of opto-electronic and electrochemical sensors.

COLL 237

Electrocatalytic behavior of in situ generated surface-bound palladium nanoparticles towards wide range of alcohol oxidation reactions

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Surface-bound palladium nanoparticles are generated through a novel in situ approach using a cationic aminosilane monolayer template. Initial electrochemical investigations of these nanoparticles revealed a highly efficient catalytic activity for many long-chain and poly alcohols including methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol, and glycerol. Cyclic voltammetry is used to determine the efficiency of these nanoparticle catalysts as well as to gain a general understanding of the kinetics and mechanisms of the various alcohol oxidations. In addition, impedance measurements are used to gain a better understanding of the process at the electrode-electrolyte interface through the analysis of an equivalent circuit. Average particle size and morphology of these nanoparticle assemblies are determined using Atomic Force Microscopy (AFM). Surface Zeta Potential measurements as well as Fe(CN)₆³⁻/⁴⁻ and Ru(NH₃)₆²⁺/³⁺ as redox probes for impedance measurement are used to track the surface charge throughout the synthesis process. Results indicate a higher catalytic affinity for poly alcohols over long-chain type alcohols.

COLL 238

Application of electron microscopy on biological samples to be prepared under critical point dryer

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This paper represents the sample preparation of biological specimens and the samples are coated with gold/palladium and viewed under SEM.

COLL 239
Application of compostable plastic materials to be degraded with compost environment standards

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This paper represents the biopolymers degraded in full-scale operations using ASTM test method standards.

COLL 240

Role of the conformational changes of the oil molecules on the protein conformational changes at oil-water interfaces

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The contributions of the time-dependent changes in oil molecules conformations on time-dependent conformational changes of proteins at oil-'protein solution' interface was studied using ATR (Attenuated Total Reflection)-FTIR spectroscopic technique. Conformational changes of Bacillus Subtilis extracellular proteins (BSEPs), Fibronectin and Bovine serum albumin (BSA) at hexane-'protein solution' system was compared. The IR spectra collected on the protein aggregate - film - formed at the hexane-'protein solution' interface demonstrated time-dependent conformational changes of the proteins through changes in the shapes and positions of the H\textsubscript{2}O-'amide I' cross peaks and the amide II peaks as a function of time (0-90\textsuperscript{th} minute). Hexane-protein intermolecular association in the film was evident as the CH stretching vibration peaks of hexane were present along with the amide peaks in all the spectra collected over a period of 90 minutes. Conformational changes of the hexane molecules, along with that of the proteins, were observed via variations (broadening and red/blue shifts) in the CH stretching vibration peaks of the CH\textsubscript{3} and the CH\textsubscript{2} groups of hexane. The red/blue shifts of the CH stretching vibration peaks of hexane were different with BSEPs, Fibronectin and BSA, further indicating that the conformational changes of hexane molecules being protein specific. As similar to the protein types considered here, at oil-'protein solution' interfaces, conformational changes of the oil molecules appears to be a regular phenomenon and possibly play a key role in regulating the protein conformational changes at Oil-Water interface. This result provide new insights onto the understanding of the role of phospholipids conformatonal changes on cell membrane protein dynamics.
Development of electrochemical materials for environment-friendly lead-free process

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This paper represents the application of electrochemical materials as lead-free soldering chemicals for electronic environment.

Effect of organic compounds on Fe(II) sorption onto clay and aluminum oxide minerals

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Microbial respiration of Fe(III)-oxides and hydroxides in suboxic and anoxic aqueous geochemical environments results in release of aqueous Fe(II) into solution. The geochemical fate of released Fe(II) is at least partially influenced by Fe(II) sorption with mineral substrates of the soil matrix. Our previous work has shown rapid formation of Fe(II)-Al(III) layered double hydroxides (Fe(II)-Al(III)-LDHs) and Fe(II)-phyllosilicate during aqueous Fe(II) sorption onto γ-Al\(_2\)O\(_3\)and clay at the near-neutral pH values typical of anoxic soil environments.\(^{1,2}\) Dissolved organic compounds, which are abundant in reducing soil environments like wetlands, may impact Fe(II) sorption behavior by interacting with Fe(II) in solution or at the surface of mineral substrates. Here, we used batch sorption studies combined with extended X-ray absorption spectroscopy to study the effect of humic acids (HA) and fulvic acids (FA) on Fe(II) sorption reactions with clay and aluminum oxide substrates at pH 7.5 under anoxic conditions over reaction times up to 3 months. We observed that the addition of organic compounds reduced the extent and rate of Fe(II) sorption onto the mineral substrates, with specific effects varying with substrate type and the type of organic material (HA or FA) added. The model systems assessed here will improve our understanding of the geochemical fate of Fe(II) in suboxic and anoxic aqueous geochemical environments.


**COLL 243**

**Development of bromoterephthalic acid for versatile preparation of TCNQ derivatives as electron acceptors**

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This paper represents the development of bromoterephthalic acid for versatile preparation of tetracyanoquinodimethanes derivatives as strong electron acceptors whose complexes are examples of electrical conductors.

**COLL 244**

**Fluorescence quenching study of small colloidal nanocrystals yields insight into surface trapping processes**

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Small colloidal semiconductor nanocrystals display interesting fluorescence properties and hold promise for next generation solid state lighting applications. These structures show both a narrow core and a broad surface emission peak. The chemical environment of the surface of these structures permits modulation of the ratio of those two peaks through which eye-pleasing white light can be created. Due to their well-defined core and surface emission bands, small nanocrystals are uniquely suited as a model system for photo physical studies. Yet few studies have taken advantage of theoretical advances in surface trapping to guide rational design of nanocrystal surfaces for white light applications.

Here we demonstrate the effects of different quenchers on the radiative properties of a variety of small nanocrystals, using steady state and time dependent fluorescence measurements. A systematic approach of comparing different ligand-quencher interactions give insight into physics of surface emission. For these studies, the effects of quenchers on small CdSe nanocrystals with different ligands are compared to their effects on small CdSe/CdS core-shell heterostructures. In addition Iodine is compared to quenchers traditionally used in nanocrystal quenching studies (ie. butylamine).
COLL 245

Gold nanoparticle-based colorimetric assay for detection of cholera toxin

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In considering food safety, there is always a need for detection of food toxins. Among different food contaminants, cholera toxin is very common. It is a protein enterotoxin produced by Vibrio cholera that can cause severe diarrhea, acidosis and can become an epidemic if treatments are not readily available. Even though it has been eliminated from developed countries, it may emerge again through imported foods from developing nations. In spite of having various analytical techniques for the detection of cholera, many of these are time-consuming, labor-intensive, and/or costly. Therefore, there is a clear need for the simple detection of cholera where any layman can use the techniques and interpret the results. In this work, we demonstrate both colorimetric and Dynamic Light Scattering (DLS) assays for cholera detection. Briefly, in the presence of cholera toxin, antibodies attached to gold nanoparticles undergo aggregation, which leads to a colorimetric change that can be visually observed. We have also used DLS to measure the size of aggregation, which correlates with the colorimetric change. In the poster, detailed results of the colorimetric and DLS assays will be presented.

COLL 246

Tuning polymeric micelle stability and drug loading with selective chemical modifications

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Polymeric micelles have been heavily investigated for their use as delivery vehicles for poorly soluble, potent chemotherapeutics. While these systems have shown clinical promise, poor stability and low drug encapsulation have hindered transfer of many formulations into the clinic. Our lab has designed a biodegradable polymer comprised of a hydrophobic copolymer backbone and a hydrophilic graft, forming a unique co-polymer, poly(D,L-lactide-co-2-methyl-2-carboxytrimethylene carbonate)-graft-poly(ethylene glycol) (P(LA-co-TMCC)-g-PEG)1. This polymer self-assembles in water to form polymeric micelles with low dispersity.
In order to make micelles with improved stability and higher drug loading, we asked how changes to both the hydrophilic corona and the hydrophobic core would affect serum stability and drug encapsulation, respectively. The free carboxylates on the TMCC of the backbone were used to chemically modify the polymer and tune its properties for drug delivery. The hydrophilic corona was modulated by controlling the number of grafted PEG chains using carbodiimide chemistry. Micelle characterization and stability studies revealed that increasing coronal PEG density prevents particle aggregation under both serum-containing conditions and through the freeze-drying process, eliminating the need for stabilizing excipients. The hydrophobic core was tuned for greater hydrophobic drug encapsulation by modifying the carboxylates on the backbone with hydrophobic groups. Combined, our polymeric micelles have superior stability and improved drug loading, creating a drug delivery system that overcomes many of the current challenges.


**Coll 247**

**Air-stable elemental copper nanoparticle synthesis by anaerobic bacteria controls size and enables scalability in aqueous solutions**

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Ultrafine, air-stable elemental copper (Cu) nanoparticles (NPs) were synthesized in aqueous solution by a microbial process using anaerobic, metal-reducing *Thermoanaerobacter* sp. X513 bacteria. Surfactants were used to biotically produce size-controllable Cu NPs with the results compared to abiotic crystals (without bacteria). Abiotic Cu crystals were formed during a 2-day incubations via chemical reduction by glucose, but the crystals exhibited a micron size with bimodal distribution with diameters of 1.54±0.34 µm (n=18) and 0.56±0.17µm (n=21). The biotic Cu crystals also were micron size (1.75±0.46 µm (n=20)) after 3-day incubations, but they were more air-stable and uniform than abiotic crystals. In situ addition of nitrilotriacetic acid as a metal chelating agent facilitated the growth of Cu NPs within 2 days and limited bimodal distribution to 70.1 ±21.3 nm (n=147) for large NPs and 2.7±0.8 nm (n=420) for small NPs, but the harvested Cu NPs were composed of Cu and Cu$_2$O mixture. Addition of capping agents including oleic acid, oleylamine, ascorbic acid, and L-cysteine resulted in well suspended colloidal Cu NPs in aqueous solution and effectively quadrupled their stability in air up to 6 hrs. The effectiveness of capping agents for suspending NPs and resistance to oxidation were quantitatively evaluated by UV-vis absorption measurements tracking the Cu localized surface plasmon resonance and time-dependent XPS studies of Cu NPs films. FTIR spectroscopy suggests that these chelating and capping agents were effectively chemisorbed on the NP surface and provided oxidation resistance in aqueous and dry condition. Finally, this process was found to be highly reproducible and scale-up conditions were evaluated in the range of 10–1,000 mL growth medium.

**COLL 248**

**Molecular dynamics simulation of dispersant activity at oil-water interface**

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Dispersants play a crucial role in the suspension polymerization process for the production of polymer resins. The dispersant package used in industry processes often involves two or more macromolecules (such as polymers or proteins). How these molecules behave at the oil-water interface is not very well understood, which hinders the development of new dispersant packages for existing or new polymer resins. In this study, we use the molecular dynamics modeling technique to simulate the activity of one dispersant package (gelatin and PADMAC) at the oil-water interface. The simulation results show that the charged amino acids in gelatin keep the gelatin at the
interface while the non-polar region is immersed in the oil phase. The PADMAC polymer is not soluble in the oil phase and stays in the aqueous phase. Strong electrostatic interactions between the cationic backbone of PADMAC and the charged groups in the gelatin anchor the PADMAC to the gelatin and therefore to the interface. This shows that PADMAC, in conjunction with gelatin, can adsorb to the oil-water interface and thus stabilize oil droplets in the suspension polymerization process. The fundamental understanding gained from this study would be useful in the design of new dispersant packages for suspension polymerization.

COLL 249

Interfacial charge transfer and reactivity of supported metal oxide nanoclusters

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Inverse catalysts, where metal oxide nanostructures are deposited onto a metal substrate, can be used as model systems to study the role of oxides in heterogeneous catalysts. Cu-based catalysts are of particular interest because they are highly active in important industrial reactions, such as the water-gas shift reaction, but their performance is strongly dependent on the Cu–metal oxide combination. In our studies, we deposit small mass-selected metal oxide clusters onto Cu(111) and investigate the metal–metal oxide interface using two-photon photoemission (2PPE). Local work function measurements show that the work function shift between clean Cu(111) and the cluster-deposited Cu(111) follows a non-linear dependence on cluster coverage. The trend in the degree of charge transfer from the copper to the oxide clusters, as seen from the work function shifts, generally follows the trend in the electron affinity of the gas-phase clusters. We also examine the chemistry of these systems toward water dissociation, a key step in the water-gas shift reaction, using temperature programmed desorption (TPD). In general, we find that the systems with less charge transfer are more active toward water dissociation.

COLL 250

Sum frequency generation at the DMSO/air interface: Theory meets experiment

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With the recent development of High Resolution Broadband Sum Frequency Generation (HR-BB-SFG) it is possible to obtain true SFG spectra with negligible instrumental line broadening. This allows quantitative analysis of the spectrum using complex Lorentzian
fitting, and through the polarization null angle (PNA) method the molecular orientation can be determined. Using the polarizability tensor and dipole moment of individual vibrational modes to construct the full hyperpolarizability tensor allows for orientational averaging of the third rank tensor without use of generalities. For both symmetric and asymmetric vibrational modes of DMSO the results of the PNA method can be recreated computationally and various experimental configurations can be tested, such as changing incident angles for both IR and visible wavelengths. The results confirm the validity of the PNA method and the polarization selection rules of SFG, as well as create a standard procedure to be used with calculated polarizability tensors and dipole moments for vibrational modes of other molecules.

**COLL 251**

**Desorption kinetics of branched alkyls through hydrogen elimination pathways on Si(100)-2x1**

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Kinetic parameters of hydrogen-elimination mediated branched alkyl desorption from Si(100)-2x1 were studied using temperature programmed desorption mass spectrometry (TPDMS). Experimental work was also accompanied by computational modeling. Branched haloalkanes predictably react with the surface to form the corresponding surface alkyl products through the cleavage of the C-X bond (X=halogen). Mass spectrometry was used to monitor desorbing products which form as a result of hydrogen elimination reaction channels. Desorption energy and pre-exponential factor kinetic parameters for the hydrogen elimination channels were measured using different kinetic models, including the Redhead analysis and the complete method by direct application of the Polanyi-Wigner equation. Values for the kinetic parameters are compared between branched alkyls having varying ratios of α to β hydrogens available for elimination. Experimental results were compared to electronic structure calculations based on conventional transition state theory for varying surface coverage and hydrogen transfer sites. General structure-activity trends for the thermal decomposition of branched alkyls with respect to the hydrogen elimination desorption channels on the silicon surface will be discussed.

**COLL 252**

**Photocatalytic activity of nanomaterial for detoxification of organic compounds**

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The acidity of Cr-incorporated Al-MCM-41 nanomaterials was investigated by adsorbing pyridine using transmission infrared spectroscopy. Both Lewis and Bronsted acid sites were found to be present as determined by corresponding IR modes on surfaces.
Adsorption of acetaldehyde was used a model compound to understand the reactivity of the nanoparticles towards catalytic degradation. During adsorption at low temperature, the acetaldehyde molecule binds through H-bonding with surface –OH groups. In addition, a fraction of acetaldehyde adsorbed through Lewis acid sites- Cr (IV) and Al (III). The combination of both H-bonded and Lewis acid sites bound acetaldehyde underwent condensation reaction forming aldol which then dehydrated at elevated temperature forming 2-butenal. Acetaldehyde underwent photodecomposition to CO₂ during photooxidation at 273 K and 173 K. This oxidation involves photoactive acetyl radical and Cr ion. A variety of condensation products also identified using TPD during photochemical reaction.

COLL 253

Incorporation of gemini surfactants into pyridinium lipoplexes enhances transfection through endosomal membrane destabilization

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Pyridinium amphiphiles – lipids, gemini surfactants, lipophilic polycations can act as efficient synthetic transfection systems with reduced toxicity in vitro and in vivo. Recently we introduced a second-generation pyridinium gemini surfactants through comprehensive tuning of the self-assembling process of these amphiphiles at the level of counterion, hydrophobic chain, added co-lipids, their nature and molar ratio. The current study presents the effects of blending these new pyridinium cationic gemini surfactants into cationic pyridinium lipid bilayers and its impact towards plasmid DNA compaction and delivery process in terms of transfection efficiency, cytotoxicity and internalization mechanism of resulted nucleic acid complexes.

COLL 254

Interfacial behaviors of fluorescent conjugated poly(diphenylacetylene) derivatives at the air-water interface

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In this work, we explored interfacial behaviors and fluorescent properties of poly(diphenylacetylene) (PDPA) derivatives as soft conjugated polymers at the air-water interface. Surface pressure-mean molecular area (π-A) isotherms and atomic force microscopy (AFM) images of the Langmuir-Blodgett (LB) [or Langmuir-Schaefer (LS)] films provided a critical finding that the spreading solution concentration and addition of amphiphilic small molecules are important factors in determining surface micelle aggregation and surface morphology. Furthermore, the stability and reversibility of
Langmuir monolayers on the water were investigated by isobaric creep measurements and compression-expansion cycles. In addition, the effects of surface morphological change on the fluorescent properties, associated with alkyl chain length and substitution position, were examined using LB (or LS) films transferred at various surface pressures.

**COLL 255**

**Au core multi-hollow shell nanoparticles: Synthetic method for controlling number of shells and gap-distance and their optical properties**

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Au nanodisk-core multi-shell nanoparticles (NDCMS-NPs) were synthesized using an Au nanodisk core as a seed to deposit a controlled number of surrounding Ag layers, followed by galvanic replacement reactions with Au ions in water. Uniform Core rigidity was found to survive during the multiple Ag coatings and galvanic replacements without structural collapse. Au NDCMS-NPs with controllable shell numbers and intershell distances exhibited unique surface plasmon mode shifts, which were found to be dependent on the thickness of the Ag layer. The number of shells was tuned by controlling the multi-step reactions from one to five. The Au core played a critical role in terms of holding the multi-shell structure during the experimental procedures. The large surface area and space in a single CMHS-NP have utility as a surface enhanced Raman scattering (SERS) substrate, nanoreactor for effective catalytic properties.
**Tunable lyotropic photonic liquid crystal based on graphene oxide**

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A direct colloidal self-assembly approach was utilized to prepare photonic crystals based on exfoliated graphene oxide (GO) in aqueous solution. The GO sheets form ordered photonic structure spontaneously without a need for multiple processing steps. The wavelength of light reflected by the GO photonic crystal dispersion can be controlled over the entire visible light spectrum simply by varying the GO concentration. The aspect ratio of the GO sheets and mediation of the inter-sheet forces are found to be the key factors influencing the stability of photonic crystal formation. The usefulness and limitation of the GO photonic crystals prepared in this study are discussed.

**Advanced methods for study of molecular organization of humic acids**

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This work deals with the conformation and molecular organization of humic acids in aqueous solutions. Humic substances have heterogeneous and polydisperse nature, therefore their secondary chemical structure has not yet been defined properly, neither has their conformational arrangement. The conformation of humic substances in the solutions is mainly stabilized by weak disperse forces, such as Van der Waals, π-π, CH-π interactions and hydrogen bonds. Humic substances in the solutions tend to form aggregates that are held together mostly by the intermolecular hydrophobic interactions. Concentration series of humic acids were prepared in three different mediums of constant ionic strength: NaOH and NaCl (prepared either by neutralization NaOH by HCl or direct dilution by solution of NaCl). Advanced methods of high-resolution ultrasound spectrometry, dynamic light scattering, laser Doppler velocimetry and micro-rheology methods have been used to determine conformation and molecular organization of humic acids. Obtained results have been compared with those of traditional methods (potentiometric determination of pH, direct conductometry, ultraviolet and visible spectroscopy, density measurement).
It was confirmed that the conformation and molecular organization of humic acids in aqueous solutions depend not only on pH of medium, but they also depend on chemical nature and concentration with the same pH. Results showed that hydrodynamic diameter of particles is significantly increasing in NaCl medium prepared by neutralization NaOH by HCl, particularly at low concentrations, which corresponds to higher values of zeta potential obtained. Concentration dependencies of ultrasonic velocity and compressibility also indicate the changes in conformation and molecular organization corresponding with results from other methods used.

**COLL 258**

**Structure and functionality of a composite photoanode for water oxidation**

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A novel composite photoanode has been developed to enable solar-driven water oxidation to produce fuel hydrogen. The photoanode was fabricated using layer-by-layer coating of a manganese-based water oxidation catalyst (WOC) on titanium dioxide (TiO2), a classic semiconductor material. The WOC is designed to structurally mimic the natural oxygen evolution complex. Its surface morphology and elemental composition were characterized after each layer of coating, using scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and x-ray diffraction (XRD). The functionality of the catalytic photoanode was assessed by cyclic voltammetry (CV), and showed excellent effectiveness towards water oxidation, both with and without illumination. The system has the potential for integration with sequestered CO2 to produce a variety of organic compounds including liquid fuels. The use of TiO2 also provides the possibility of incorporating other novel materials in the future, to design highly efficient solar harvesting systems with broader absorption spectra than currently available.

**COLL 259**

**Facile solvothermal synthesis of NIR absorbing CsxWO3 nanorods and their water based sol-gel coatings**

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In recent years, with the increase of environmental and energy saving concern, there has been a great demand for transparent and solar heat shielding coatings for windows of buildings and automotives. Application of heat shielding materials requires high visible transparency and excellent near-infrared (780-2500nm) shielding ability. In this work, we have reported facile solvothermal synthesis of NIR absorbing CsxWO3 via
benzyl alcohol route. Hexagonal CsₓWO₃ nanorods with average size of 80 nm were synthesized in 2 hours reaction time at low reaction temperature (240°C) in the presence of oleic acid capping agent. The well-dispersed CsₓWO₃ nanorod in a stable water based sol-gel coating has been prepared. The result showed high transparency (ca. 80-90%) in the visible light with strong near infrared (NIR) light shielding (80-90%). The practical application of this work can provide internal comfort for automotives and buildings as well as reduces the energy consumption for air conditioning that should result in a decrease of carbon dioxide emission.

COLL 260

Characterization of oxidized and pristine carbon nanotube stabilized Pickering emulsion

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Multiwalled carbon nanotubes MWNT's in biphasic systems have recently gained attention as Pickering emulsion stabilizers in the areas of underground oil recovery and heterogeneous catalyst supports due to their ability to undergo functionalization and tune the surface chemistry while maintaining the nanotube's unique electronic and physical properties. While a great deal of literature exists for nanoparticle stabilized Pickering emulsions, very little is known about the fundamental behavior of MWNT's as Pickering emulsion stabilizers. In this study, the emulsion type and emulsion droplet size were varied by modifying the hydrophobicity of the MWNTs. The surface hydrophilicity was altered by introducing carboxylic groups as well as by adding a hydrophilizing agent. It was found that the oil-to-water ratio at which the emulsion type inverts changes depending on the degree of hydrophobicity of the MWNTs, with MWNTs of intermediate hydrophobicity changing emulsion type close to equal volumes of oil to water. Regardless of the MWNT's hydrophobicity, emulsion droplet size was found to decrease as the concentration of MWNTs increased, while the total oil/water interfacial area in the system increased. It was found that as more MWNT's were added to the system, the effective interfacial area stabilized per MWNTs introduced reached a plateau, indicating the potential formation of multiple layers of MWNTs at the water/oil interface. Optical microscopy and acoustic spectroscopy were used to characterize the Pickering emulsions created. Temperature programmed desorption was used to quantify the number of functional groups, which were responsible for changing the MWNT's hydrophobicity.

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Affinity tunable host-guest dendrimers exploited to trigger receptor clustering induced VEGF signaling pathway on molecular printboard
Cell surface receptors play a very important role in monitoring extracellular functions as well as coordinating intracellular events via transduction of external information [1]. Most of the growth factors present in the cell environment also elicit their activity via these surface receptors [2]. Multivalent ligands are reported to induce the clustering of these receptors to trigger the localized activation of growth factors which are otherwise highly diffusible and difficult to segregate in \textit{in vivo} conditions [3].

With the advances in surface fabrication techniques different ligands can be fabricated on the surface to gain spatial and temporal control over growth factor activity known as “preorganization of growth factor” [4][5]. Moreover electrochemical stimulus can also be used to elicit the localized response of growth factor [6][7].

We present dendrimer functionalized nano-platforms to preorganize the VEGF mediated bio signaling complex on molecular print board via non covalent host-guest interactions. Recently a peptide sequence (EYPD) is reported which is specific for α9β1 integrin receptors known to involve in eliciting VEGF activity [8]. Thus we hypothesized that if we present this peptide in a multivalent fashion we will be able to cluster these integrin receptors which will act as a trigger for recruitment of VEGF at these clustered sites. We envisioned that this multivalency can also help to stabilize this construct on β-CD monolayer (molecular print board) by host-guest interactions between tyrosine present in peptide and cup shaped β-CD molecules.

Moreover this supramolecular fabrication technique gave us a unique access whereby modifying dendrimer design, we were able to tune the affinity of dendrimers with molecular print board.

References


Interactions between cerium oxide nanoparticles and biochar nanoparticles

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The stability of engineered nanoparticles (NPs) in soil is a subject of intense interest due to the potential hazardous effects of NPs in the environment. Pyrogenic biomass materials from wildfires (chars) are ubiquitous constituents of soil, and pyrolyzed biomass wastes (biochars) are attracting interest for improving soil fertility in agriculture and assisting in soil remediation. In this study, heteroaggregation of cerium oxide nanoparticles (CeO$_2$-NPs) and biochar nanoparticles (biochar-NPs) was investigated in DI water at pH 5.6 using time-resolved dynamic light scattering. Biochar-NPs of fairly uniform size (30−220 nm) were produced by filtration of an aqueous suspension of a pulverized pecan shell biochar produced at 500 °C. The zeta potentials of CeO$_2$- and biochar-NPs were 45 and −23 mV, respectively, at pH 5.6 and both NPs were stable to homoaggregation. To examine the influence of biochar-NPs on the colloidal stability of CeO$_2$-NPs, the concentrations of CeO$_2$-NP and biochar-NP suspensions were adjusted so that the scattered light intensities of biochar-NPs were less than 8% of that of CeO$_2$-NPs. At low biochar-NP/CeO$_2$-NP ratios, biochar-NPs had no effect on the hydrodynamic diameter of CeO$_2$-NPs. However, as the biochar-NP/CeO$_2$-NP ratio increased, the initial growth rate of CeO$_2$-NPs increased accordingly and reached a maximum value of $\sim 30$ nm/min due to heteroaggregation at the "optimum" biochar-NP/CeO$_2$-NP ratio. With further increase in the biochar-NP/CeO$_2$-NP ratio above the optimum value, the growth rate of CeO$_2$-NPs decreased eventually to zero at high biochar-NP/CeO$_2$-NP ratios. The reversibility of heteroaggregation was tested at the optimum biochar-NP/CeO$_2$-NP ratio by increasing pH from 5.6 to 11, where the zeta potentials of CeO$_2$-NPs and biochar-NPs declined to $-20$ and $-42$ mV, respectively. Although the heteroaggregation ceased when pH increased, no disaggregation was observed at pH 11, despite the high electrostatic repulsion presumably existing between CeO$_2$-NPs and biochar-NPs, indicating poor reversibility. The underlying cause(s) will be discussed.

Microfluidic encapsulation of colloidal photonic structures toward photonic ink capsules
Colloidal particles can be assembled to form crystalline or amorphous structures which exhibit their own photonic effects; crystalline shows strong iridescent colors and amorphous structure shows non-iridescent colors. Such colloidal photonic structures are promising as new class of photonic materials and color pigments. However, controlled formation of crystalline and amorphous structures and their encapsulation into 'ink' capsule still remain important challenge.

Here, we report a microfluidic approach to create photonic capsules containing colloidal structures. With a glass capillary device, an aqueous suspension of polystyrene particles is encapsulated with ultra-thin oil shell in a continuous water phase, thereby resulting in water-in-oil-in-water (W/O/W) double-emulsion drops. The drops are then subjected to hypertonic condition, which pumps water out through the thin shell, thereby leading to concentration of the particles in the innermost water drops. The concentration rate strongly influences optical appearance of the drops, where the rate is precisely controlled by adjusting osmotic pressure difference. At low pressure difference, colloidal particles are slowly concentrated, thereby yielding colloidal crystals in the drops; the drops exhibit sparkling color pattern. Stepwise increase of external osmotic pressure can yield highly concentrated colloids, while maintaining crystalline phase. At high pressure difference, the particles are quickly concentrated, which suppresses crystallization of the particles; the drops still show colors but no sparkling pattern. This is attributed to short-range order; glass-like packing of uniform colloids has consistent interparticle distance, which can provide less-iridescent structural color. As an oil phase, a photocurable resin can be used, which enables the polymerization of ultra-thin shell after formation of crystalline or glass photonic structures, thereby stabilizing the photonic structures. The photonic microcapsules, containing colloidal crystalline or glass, can be used as building block to construct photonic devices or aesthetic color coating.

COLL 264

Effect of block composition on micelle size and steric stabilizer layer thickness: Polystyrene-based diblock copolymers are effective dispersants for carbon black particles in n-dodecane

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Three polystyrene-based diblock copolymers are evaluated as dispersants for carbon black particles in n-dodecane. Each diblock copolymer forms polystyrene-core micelles in this solvent as judged by variable temperature $^1$H NMR spectroscopy, DLS, TEM and SAXS. According to a UV spectroscopy supernatant depletion assay, these diblock
copolymer micelles adsorb onto the carbon black particles to form a relatively thick stabilizer layer. Consequently, the effective density of the sterically-stabilized carbon black particles is substantially lower than that of the pristine carbon black particles (1.89 g cm\(^{-3}\) as judged by helium pyconometry). In each case, the effective particle density can be determined by determining the particle velocity in both n-dodecane and d\(_{26}\)-n-dodecane via analytical centrifugation. Using this corrected particle density enables the true particle size distributions of these carbon black dispersions to be assessed and the thickness of the steric stabilizer layer can be estimated. It is found that the mean particle diameter of the carbon black is close to its primary grain size of 74 nm (as judged by BET nitrogen adsorption studies), which suggests a relatively high degree of dispersion for this model colloidal substrate.

**COLL 265**

**Enantioselective separation via DNA-based chiral selectors**

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DNA-based chiral selectors were constructed via the specific interactions among metal ions, DNA and the drug enantiomers. Metal ions including Mg\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Ag\(^{+}\) and Pt\(^{2+}\) are utilized to regulate the enantiomeric resolution through different coordination modes with DNA. For the chiral ofloxacin, DNA-Cu(II) complexes exhibit the highest enantioselectivities at the [Cu\(^{2+}\)]/base ratio of 0.1, i.e., the enantiomeric excess can reach to 59% in R-enantiomer after being adsorbed by RET-Cu(II) complex. Through programming DNA sequences, the maximum S- and R-enantiomer adsorption capacities on the Cu\(^{II}\)-DNA complex can be increased. This work illustrates a novel promising route to construct DNA-based chiral selectors towards certain drug enantiomers through the programmable enantioselective recognition on the basis of DNA chirality and the specific binding of transition metal ions.

**COLL 266**

**Infrared invisibility stickers inspired by cephalopods**

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Cephalopods are known for their remarkable camouflage abilities. They can modify their skin's coloration, texture, pattern, and reflectivity to blend into the surrounding environment. We have drawn inspiration from nanostructures found in cephalopod skin to fabricate dynamically tunable biomimetic camouflage coatings on transparent and flexible substrates. Our substrates can adhere to arbitrary surfaces, and we can reversibly modulate their reflectance from the visible to the near infrared regions of the electromagnetic spectrum. Thus, common objects can be endowed with tunable
camouflage capabilities. Our work represents a first step towards a disposable, dynamically reconfigurable infrared stealth technology.

COLL 267

Flexible, stretchable, and reconfigurable RF electronic devices enabled by control of gallium liquid metal alloy surface chemistry

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There is tremendous interest in leveraging the unique properties of gallium liquid metal alloys (GaLMAs) to develop flexible, stretchable, conformal and reconfigurable RF electronic devices. These properties are difficult or impossible to achieve using traditional dynamic tuning platforms such as microelectromechanical switching (MEMS) or electronic switching (solid state components). Use of tunable antennae and/or structurally integrated stretchable electronic components to support or replace traditional electronic materials offers critical advantages including: ultra-broadband response, dynamically tuned RF functional window, multi-level switching, directional steerability, and on-demand reconfiguration.

The work presented here details efforts to manipulate the surface chemistry of gallium liquid metal alloys (GaLMAs) with the purpose of controlling flow to alter the electrical and electromagnetic response of various RF microfluidic electronic devices. Under ambient conditions, the surface of a GaLMA spontaneously develops a thin layer of Ga$_2$O$_3$ that imparts structural stability to deposited metal droplets and increases the stickiness of the alloy to surfaces. This property is potentially useful for self-healing applications where passivating surface oxidation of the alloy can prevent significant material leakage from a damaged circuit and enable quick reconnection; however, challenges arise for reconfigurable electronics applications where metal oxide residue can interfere with actuation between multiple circuit elements. Previous work by Dickey and coworkers (North Carolina State University) demonstrates that surface oxides of liquid metals are reduced in the presence of HCl, either in vapor form or after diffusion through a PDMS membrane. Reduction of the oxide layer results in alloy dewetting and a fully liquid droplet forming. This work demonstrates the exquisite control obtained by using proton exchange membranes as the interfacing layer with the GaLMA materials that greatly reduce the need for the direct presence of caustic (HCl) materials. We show how various film treatments influence the wettability of deposited GaLMA, with potential implications for channel filling/evacuation within proposed RF electronic devices.

COLL 268

Nanotemplates with electrospray deposition and atomic layer deposition
Metal nanoparticles have shown great catalytic activity at low temperatures for numerous reactions, but sintering of the nanoparticles remains a huge hurdle for practical applications. To overcome sintering, we are developing a surface modification that results in metal nanoparticles physically isolated in nanosized craters. For the first time, gold nanoparticles encapsulated in block copolymer reverse micelles were deposited on a titania surface in vacuum using electrospray deposition. Additional titanium dioxide was deposited using atomic layer deposition with the polymers serving as templates to prevent thin film growth on the nanoparticles. Atomic oxygen successfully removed the polymer to leave a surface patterned with irregular craters as shown in scanning electron microscopy images. X-ray photoelectron spectroscopy was used to confirm nanoparticle deposition, thin film growth, and polymer removal. The applicability of this surface modification scheme with other organic functionalized nanoparticles will be discussed.

Self-assembly of de-novo synthesized functionalized pyrenes on coinage metal surfaces

Supramolecular architectures on metallic surfaces provide multiple prospects for the engineering of novel nanostructured materials. Of particular interest are building blocks with inherent functional properties, such as single molecule magnets or photoactive groups. Here we report a scanning tunneling microscopy study on the self-assembly of a family of pyridil- and phenyl-functionalized pyrenes, including an optically active backbone molecule already used in commercial dyes, on Ag(111) and Cu(111). By systematically changing the molecular functionalization and symmetry, different supramolecular synthons are expressed.
Phenyl-substituents result in a uniform pyrene distribution on the surface, whereas pyridil-terminations drive the formation of different regular 2D networks that may surprisingly include metal-organic binding motifs engaging Ag adatoms. The electronic features of these systems were probed by scanning tunneling spectroscopy.
Dip-pen nanolithography for integrating nanomaterials

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Dip-pen nanolithography (DPN) is an atomic force microscopy-based nanolithography technique for patterning a wide range of materials at addressable locations with nanoscale precision. The compatibility of DPN with a variety of “inks” and surfaces makes it an effective tool for integrating soft and hard materials on the nanoscale. Here, we present the effects of ink properties (concentration, viscosity, hydrophilicity/hydrophobicity), patterning velocities, and surface functionalization on the direct nanoscale patterning of nanocrystals inks using DPN. Moreover, we utilize DPN in conjunction with traditional lithographic techniques to build hierarchically nano/mesostructured materials with new functionalities. By combining the imaging and writing components of DPN, we demonstrate for the first time, the ability to accurately position nanocrystals on complex, pre-fabricated, 3D sub-micron nanostructures. For this, we employ DPN to place core/shell quantum dots (down to the few-quantum dot level) on silicon nanodisk antennas to subsequently study the emission enhancement effects.

Importance of Au/oxide interfaces for the water-gas shift reaction: A computational study

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The water gas shift (WGS) reaction is relevant to a spectrum of industrially-important catalytic processes, including the manufacture of hydrogen and processing of both hydrocarbons and biomass-derived chemicals. In addition, it serves as a useful model chemistry to investigate catalytic reactions at metal/oxide interfaces. Recently, oxide-supported Au catalysts have gained attention for low-temperature WGS reactions due to their surprising properties as compared to bulk Au catalysts, but the detailed mechanisms of how these catalysts promote WGS remain under debate. In this study, we perform extensive density functional theory (DFT) calculations at the generalized gradient approximation (PW91) level, as well as at the hybrid level (HSE06). A supported gold nano-wire on an extended MgO(100) slab model is used as an initial
model to explore the reaction mechanism of WGS at Au/oxide interface; based on the results of previous experimental studies, this is believed to be a plausible candidate for the active site. Compared to the previous theoretical study on Au(111) itself, a major difference for the reaction at the Au/MgO interface is that the water dissociation barrier is dramatically decreased from > 2 eV on Au(111) to essentially zero at the Au/MgO interface. Among the previously proposed redox, carboxyl and formate mechanisms, the carboxyl mechanism is found to be the most plausible, with the formation of COOH having the highest barrier at ~0.8 eV. Based on these DFT-calculated barriers and appropriate entropy estimates, a two-site micro-kinetic model was built at Au/MgO interface. Kinetic control analysis shows that COOH formation is indeed the rate-determining step. The competitive adsorption between CO and H at the interface is also found to strongly influence the reaction kinetics. Using this model, together with the results of additional DFT calculations of Au nanowires on other oxide substrates, we conclude with a discussion of how changing the nature of the oxide support can influence trends in the reaction activity.

COLL 272

Mixed polystyrene-block-poly(4-vinylpyridine) and polyacrylamide brush for triggered hydrophobic-to-hydrophilic switching

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The discovery of different aspects of polymer brush synthesis, properties, and applications have resulted in a rapidly developing interest in the field, namely switchable systems. So far, researchers have been able to fabricate triggered switching with the use of common transition selective solvents which have brought about advances in responsive systems like self-cleaning devices. Although these systems have immense potential, the use of a selective solvent restricts further growth as only limited sets of polymers have common selective solvents. The objective of our work is to investigate hydrophilic-to-hydrophobic switching behavior of mixed polystyrene-block-poly(4-vinylpyridine) (PS-P4VP) and polyacrylamide (PAAm) mosaic systems using a common nonselective solvent. The PS-P4VP mosaic brush is prepared by incorporating supramolecular block copolymer assemblies (SMA) onto (p-bromophenyl)-trimethoxysilane modified Si-wafers. SMAs are hybrid materials which are characterized by the ability of one block selectively interacting with a low molecular additive; in our case, 2-(4’-hydroxybenzeneazo) benzoic acid additive (HABA) H-bonding with P4VP block of PS-P4VP, or PS as additive being miscible with the PS block of PS-P4VP. The SMA can form well-ordered arrays of nanoscopic pores upon selective extraction of the HABA or PS additive, which allows for the “grafting to” of PS-P4VP mosaic brush. PAAm is then “grafted through” via photoinitiation in between the PS-P4VP mosaic brush. The systems are characterized via atomic force microscopy (AFM), null ellipsometry and contact angle measurements. Surface adhesion properties are investigated via colloidal probe AFM measurements and biological cell adhesion
response is measured by bioluminescence of *Escherichia coli* and *Salmonella typhimurium* cells.

**COLL 273**

**Nanoscale positioning of multiple proteins by scanning near-field photolithography**

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The patterning of proteins on sub-micrometer length-scales remains challenging. Key issues include the need to eliminate non-specific adsorption, the susceptibility of proteins to conformational change at interfaces, the difficulties associated with ensuring site-specific attachment and the lack of reliable tools to enable the arbitrary patterning of multiple different protein components.

Here we present a simple, generic method for the positioning of one or more proteins on a surface that combines top-down (lithographic) definition of structures with bottom-up control of chemical reactivity. A monolayer of an aminosilane with a photocleavable nitrophenyl ethoxycarbonyl protecting group that is functionalised with an oligo(ethylene glycol) substituent is exposed to UV light, causing removal of the protein-resistant group. An amine is exposed that may be used to direct protein immobilisation or for further post-modification, for example attachment of nitrilotriacetic acid (NTA) containing ligands for site-specific immobilisation of biomolecules. Surface patterning has been done using mask-based exposure and, for nanopatterning and, at the nanometer scale, by scanning near-field photolithography (SNP) and interferometric lithography. SNP enables lithography to be performed under ambient or liquid conditions and the utilisation of light as the fabrication medium allows for the use of photochemical methods without damaging the protein. Two component patterns may be fabricated very simply. Features may be written by exposure of the photo-active silane to the near-field of the SNOM probe, and then functionalised with protein. The sample may then be patterned a further time, and the new features functionalised with a second protein. The functionality and specificity of these structures have been confirmed using spectroscopic confocal microscopy and AFM. For example, green fluorescent protein (GFP) and yellow fluorescent protein (YFP), molecules with emission maxima too close for separation using a filter, may be readily distinguished in spectroscopic imaging and the selectivity of placement at the nanoscale confirmed.

**COLL 274**

**TheraBlob for ultrasound-enabled ablation therapy**
The use of ultrasound to treat tumors has been investigated in the prostate, the liver, the kidney, the brain, and for various eye conditions. Despite some promising results, current approaches remain highly dependent on operator skill, and cannot treat many tumors because of the lack of précised approach to the zone of necrosis. In this work, we seek to maximally exploit three distinct properties of therapeutic ultrasound that possess new synergistic potential: cavitation/sonoporation in conjunction with novel anticancer prodrug nanobubbles (TheraBlob), enhanced tissue penetration by drug/prodrug nanoparticles and thermal effects of ultrasound.

An innovative sn-2 lipase-labile prodrug of baxoretene (Targetrin, a known RXR inhibitor) was synthesized to protect and retain the compound in the particle during circulatory transit until it is liberated and converted to the active compound by intracellular phospholipases within the target cell. TheraBlob possesses C₃F₈ in the core of the particles, and uniquely self-assembled into nanoblobs (hydrodynamic particle size: ∼100nm) directly from the amphiphilic-lipid-prodrug molecule to avoid the encapsulation of free drug into the nanoparticles. The lipid surface interacts with the cellular bilayer to undergo hemifusion (ATP-dependent way) followed by the bursting of the construct with thermal energy transmitted through US ablation. Dynamic light scattering, zeta potential and optical analysis indicated remarkable stability of prepared TheraBlob particles. Upon treatment with HepG2 cells in presence and absence of US, cell viability was measured using Trypan Blue and MTT assay at varying time points. Results indicated statistically significant cellular mortality (∼30 %) for US exposed cells by stimuli-triggered delivery of Therablobs. Ex-vivo experiments on pig liver tissues showed highly localised necrosis patterns on treated site to promise a novel pro-drug mediated cancer-chemotherapy enabled by US ablation. This research may offer the potential to overcome the shortcomings associated with other forms of targeted drug delivery and thermal therapy.

COLL 275

**Improved biosensing utilizing LSPR of metal nanoparticles both in solution and on solid substrate**

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Nanoparticles of different shape and size have been employed for chemical and biological sensing[1]. The sensing principle employed in these experiments relies on the high sensitivity of the localized surface plasmon resonance (LSPR) of noble metal
nanoparticles to local changes in dielectric constant. Herein, we describe the development of improved nanostar and nanocage LSPR biosensors both in solution and on a solid support. Bulk, solution phase biosensing with complex nanostructures is restricted mainly due to the presence of capping agents on the surface of the nanoparticles, preventing the binding of biological molecules of interest. Our approach of removing the capping agent from the surface of gold nanostars not only shows a high refractive index sensitivity of 456 nm/RIU, but also a large red shifts of ∼100 nm due to the addition of prostate specific antigen (PSA) antibody and antigen. On the other hand, some applications require surface-bound arrays that can be interfaced with on-chip devices. Here, we have carried out a galvanic ion replacement reaction [2] on an array of cylindrical silver nanoparticles to produce cage-like gold nanoparticles. It is expected that hollow nanoparticles will have higher refractive index sensitivity when compared to the solid nanoparticles [3]. In the first step, hole-mask colloidal lithography (HCL) is used to prepare silver nanoparticle arrays on a glass substrate with precisely controlled shape, size [4]. Then a galvanic replacement reaction between the silver nanoparticles and gold salt (HAuCl₄) in solution is carried out to hollow out the silver nanoparticles and obtain an array of the gold nanocage structures. The nanoparticle array was characterized using transmission electron microscopy (TEM) at different stages of the galvanic ion replacement reaction. In addition, we explore the LSPR sensitivity of gold nanocages to changes in bulk refractive index compared with solid gold nanoparticle (HCL) arrays.


COLL 276

Hemozoin derived energetic nanomaterials

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For energetic aluminum nanomaterials (nAl), the choice of oxidizing material represents a significant challenge to achieving maximum energy output. Ideally, the correct combination of oxidizer and nAl fuel will lead to the total release of its theoretical amount of energy. In reality though, the actual energy released is much less than the theoretical amount and is highly dependent upon balancing the oxidizer properties
(redox potential, size, composition, and combustion enthalpy) with the mass transport/diffusion of components. Empirically, the best oxidizing materials to date for nAl have included a handful of nanometer sized metal oxides (CuO, Fe$_3$O$_4$, FeO(OH), MnO), traditional chemical oxidizing agents (NH$_4$ClO$_4$, H$_2$O$_2$), and in a few cases fluorinated polymers. Some of these materials are hazardous and unstable for use in the development of energetic materials. Alternatively, nature offers an abundant source of potentially new components that exhibit unique structures, properties, and activities that rival man-made materials for use in energetic applications. We recently demonstrated the use of a bio-enabled assembly approach to increase the combustion kinetics of nAl. Here we explore the use of hemozoin crystals formed in vivo by the Plasmodium falciparum parasite, the causative agent of malaria, as an oxidizing material for nAl. We have created a bio-inspired nanomaterial composite that is highly energetic and reactive based on a hemozoin-nAl complex. Our results demonstrate that hemozoin rapidly oxidizes the nAl fuel to release large amounts of energy by using high speed video and differential scanning calorimetry.

**COLL 277**

One-pot synthesis of thermally responsive carbon nanoparticles for image guided therapy of melanoma

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Engineering smart stimuli responsive nanoplatforms is of paramount importance to improve sustainable targeted delivery for therapeutic and diagnostic applications. Such engineered nanoplatforms maximize therapeutic index of a drug by improving their efficacy via controlled release and enhanced accumulation at the target site. Here, we have microwave synthesized novel thermally responsive polymer coated carbon nanoparticles (CNP) with multifunctional properties capable of being imaged, loaded with drug and targeted to a specific pathophysiological region of interest. Commercial food grade molasses was used to produce the CNPs (10 – 30 nm), which were further surface passivated with poly(N-isopropylacrylamide) (PNIPAM). An intriguing aspect of the surface passivation with PNIPAM is the tunability of optical fluorescence properties within 650-850 nm which is ideal for in vivo applications (deeper penetration and low light scattering). The PNIPAM permits the localized release of therapeutics triggered by increased temperature when CNP absorbs near infrared radiation (NIR). CNPs were characterized by dynamic light scattering, zeta potential measurement, Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy, Transmission Electron Microscopy and Raman Spectroscopy. Tumor necrosis factor alpha (TNF-α) inhibitor drug, pentoxifylline (PTX) was incorporated in PNIPAM coated CNPs and investigated for anti-proliferative effect on the melanoma cell line, C32, in presence and absence of
near infrared radiation using XTT method. Drug loading efficiency and release kinetics will be presented which entails dissolution studies at various physiologically relevant temperature and pH levels. Two photon fluorescence microscopy and confocal Raman imaging were employed to monitor drug release and uptake of CNPs. Engineered thermally responsive polymer coated CNPs have immense potential to revolutionize thermally-based medical therapies to achieve desirable pharmacokinetic properties, optimal dosing, reduced off-target toxicity and stimulus-enhanced accumulation of therapeutics at target site with non-invasive monitoring.

COLL 278

Gold-engineered nanoparticles with distinct surface chemistries alter gene expression in Daphnia magna gut

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Nanoparticles are more reactive substances than their bulky counterparts due to their surface to volume ratio, it is estimated that entrance of nanoparticles into aquatic environments may have the potential to be deleterious to aquatic biota. Therefore the potential presence of nanomaterials entering aquatic environments from industry and other sources has raised environmental concern worldwide. In addition surface chemistry attached to nanoparticles entering in the aquatic environment may play a role in their toxicity and interaction with the cellular chemistry of aquatic organisms, yet it is unclear the nature of this interaction. Interaction of nanoparticles and aquatic species is widely reported. The freshwater crustacean, Daphnia magna interacts with nanomaterials through their gastrointestinal tract as they ingest particulates either from the water or the sediment. The objective of this project was to monitor the interaction of gold-engineered nanoparticles with distinct surface chemistries within the gut of D. magna by measuring the level of expression of genes associated with oxidative stress and evaluating the production of reactive oxygen species (ROS). Our outcomes demonstrated that sublethal concentrations of gold-engineered nanoparticles altered the expression of glutathione S-transferase and heat shock protein 70 genes and elicited a strong production of ROS after 24 hours exposure. This change in expression and ROS production is strongly associated with the surface charge of nanoparticles and their concentration. At higher concentrations, positively charged gold nanoparticles induced GST and HSP70 gene expression as well as ROS generation. Interestingly, the expression levels of catalase did not change across the nanoparticle treatments at any concentration. Additionally, negatively charged gold nanoparticles induced low levels of GST, CAT, and HSP70 gene expression and ROS production. Overall, the outcome of this study informs us that it is possible to evaluate gene expression at a fine scale in the
D. magna gut using an in vivo study and that the surface chemistry plays an important role in the interaction of the nanoparticles and the gut of aquatic crustaceans. These findings contribute to expand our general knowledge about the interactions between aquatic living systems and engineered nanoparticles.

**COLL 279**

**Systems biology approaches reveal low-dose effects of dendrimers**

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To date, most in vitro toxicological studies of nanoparticles are based on the assessment of acute cytotoxicity. Few studies have focused on changes in gene expression, in particular at low (non-cytotoxic) doses of nanoparticles. Here we exposed primary human bronchial epithelial cells (PBEC) to generation 4 polyamidoamine (PAMAM) dendrimers with neutral (OH) or positive (NH₂) terminating groups and evaluated transcriptomics using next generation sequencing (RNA Seq) technology. First, dose-response studies using the Lactate Dehydrogenase assay (LDH) were conducted in order to elucidate the dose range at which acute cytotoxicity was elicited in PBECs. Non-cytotoxic doses (48 h exposure) were selected for subsequent experiments. Using FITC-labeled PAMAMs, we showed that the majority of the nanoparticles were localized in perinuclear lysosomes. The uptake of PAMAMs appeared to occur through an active mechanism and PAMAM-NH₂ were internalized to a greater degree than PAMAM-OH. PAMAM-NH₂ but not PAMAM-OH were found to induce changes in gene transcription even at low doses when no overt cell death was observed. Notably, significant down-regulation of cell cycle-related genes was detected by Gene Ontology (GO) enrichment analysis. The latter data were corroborated by experiments showing that PAMAM-NH₂ treatment leads to cell cycle arrest in PBECs. Taken together, we have demonstrated that low doses of cationic dendrimers alter gene expression in human lung cells. This study indicates that systems biology and computational approaches can aid in the prediction of nanomaterial toxicity and may uncover the underlying mechanism of cellular responses. Further work is warranted to address biological effects of nanomaterials occurring at low doses of exposure, in order to understand the effects of these materials.

**COLL 280**

**Cellular uptake of polymer coated gold nanoparticles with tailored hydrophilic-to-hydrophobic ratio**
The understanding of the interaction between nanoparticles and cells is of crucial importance for many applications. Gold nanoparticles have gained popularity as model nanoparticles and as therapeutic nanocarriers. Recent observations in biological systems suggest that changing size, shape and surface coating of gold nanoparticles can affect their nonspecific uptake in cells. However, little has been reported on how cellular uptake of gold nanoparticles can be influenced by hydrophobicity. In our work, we investigate the effect of hydrophobic/hydrophilic balance on the uptake of polymer coated gold nanoparticles by dendritic cells (DCs). DCs are the most important class of antigen presenting cells of our immune system. Polymers with varying hydrophilic-to-hydrophobic ratio were synthesized via Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization, using different monomer ratios of 2-hydroxyethylacrylate to methoxyethylacrylate. Surface modification of citrate-stabilized gold nanoparticles with polymers was achieved by spontaneous ligand exchange in aqueous medium. After separation of free polymers from gold nanoparticles by centrifugation, 4 types of polymers coated gold nanoparticles with increasing hydrophobicity were obtained. Transmission electron microscopy (TEM) revealed monodisperse nanoparticles with a core size of 13 nm, and a distinct corona surrounding the gold nanoparticles, thereby indicating the successful modification with polymers. Mouse dendritic cells (i.e. DC2.4) were used to investigate the difference in cellular uptake of the 4 types of polymer-coated gold nanoparticles. After overnight incubation with the gold nanoparticles, cellular uptake of nanoparticles was analyzed via flow cytometry by measuring the shift in side scatter that is caused by internalized or cell surface bound gold nanoparticles. Focused ion beam scanning electron microscopy was further used to confirm the intracellular localization of the nanoparticles. A strong influence of the polymer coating on the cellular uptake was observed, with higher percentages of nanoparticles positive cells with increasing content of the hydrophobic methoxyethylacrylate comonomer in the polymer coating.

COLL 281

Competitive protein adsorption onto functional polymeric materials: The case of core-shell microgels

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Understanding protein adsorption onto polymeric nanomaterials is of central importance in biotechnology, tissue engineering, and nanomedicine. Despite considerable efforts in synthesis of "smart" polymeric materials during the last decades the process of
protein adsorption is still not fully understood. Furthermore, there is no consensus in literature what type of driving forces (e.g. electrostatics, counter ion release, hydrophobic effects) dominate the adsorption of bio-macromolecules. The interplay of different forces becomes even more pronounced when mixtures of bio-macromolecules are considered i.e. the case of competitive adsorption. We have studied the uptake of lysozyme, cytochrome c & RNAse A onto a negatively charged core-shell micro-gel by isothermal titration calorimetry and a fluorescence based method with varying salt concentration. We were able to fit the adsorption isotherms with a new model derived from an excluded volume approach (EV-model). Compared with the classical Langmuir type approach the EV-model also takes electrostatics and binding energies specific for each protein into account. Moreover, it can reproduce the competitive uptake of binary mixtures and can easily be expanded for multicomponent mixtures. Together with further experiments and the EV-model we hope to get an in-depth understanding of protein adsorption on a more qualitative and predictive level.

Figure: General concept: Adsorption of proteins onto micro-gels studied under influence of salt, temperature and also binary mixtures for competitive adsorption.

**COLL 282**

**Stepwise and epitaxial growth of DNA-programmable nanoparticle superlattices**

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Many researchers are interested in developing methods for rationally assembling nanoparticle building blocks into periodic lattices. These superlattices could in principle be used to create designer materials with unique properties, useful in optics, biomedicine, energy, and catalysis. DNA is a particularly attractive ligand for the programmable assembly of nanoparticles, as synthetically tunable variations in nucleotide sequence allow for precise engineering of the nanoparticle hydrodynamic radius and hybridization properties. These factors, in turn, dictate the crystallographic symmetry and lattice parameter of the assembly. Although superlattices with diverse geometries can be assembled in solution, the incorporation of specific bonding interactions between particle building blocks and a substrate would significantly enhance control over the crystal growth process. Herein, we use a stepwise growth process to systematically study and control the evolution of a bcc crystalline thin-film comprised of DNA-functionalized nanoparticle building blocks on a complementary DNA substrate. We examine crystal growth as a function of temperature, number of layers, and substrate-particle bonding interactions. Importantly, the judicious choice of DNA interconnects allows one to tune the interfacial energy between various crystal planes and the substrate, and thereby control crystal orientation and size in a stepwise fashion using chemically programmable attractive forces. We further demonstrate that such assemblies can be grown epitaxially on lithographically patterned templates, eliminating grain boundaries and enabling fine control over orientation and size of assemblies up to thousands of square micrometers. The effects of drying on the superlattice structure are examined; surprisingly, this allows for a reversible contraction and expansion of the colloidal crystal with a greater than 60% decrease in the volume of the lattice. Ultimately, this work will be important for the development of on-chip material platforms that take advantage of the periodicity and/or controlled density of the inorganic core, such as optical metamaterials, photonic crystals and heterogeneous catalysts.

COLL 283

Polydopamine thin film polymerization and electrodeposition for the fabrication of DNA-functionalized microarrays, nanoparticles, and nanorings

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Polydopamine (PDA) thin films were fabricated from dopamine solutions either by a single-step polymerization–deposition method or by a controlled electrodeposition process and then employed in the construction of DNA-functionalized microelectrode arrays, nanoring arrays and magnetic nanoparticles for biosensing applications. While the bulk self-polymerization of dopamine monomers occurred in basic aqueous dopamine solutions (pH 8.5), polydopamine monolayers could be electrodeposited and
patterned on the micron lengthscale from slightly acidic solutions (pH 6.5) by an electrochemically induced interfacial pH change. PDA multilayers with thicknesses varying from 1 to 5 nm were deposited and characterized from with a combination of electrochemistry, scanning angle surface plasmon resonance (SPR) and atomic force microscopy. DNA functionalization was accomplished by the reaction of amine-terminated single-stranded DNA (ssDNA) oligonucleotides with PDA-modified gold thin film microarray elements; these microarrays were subsequently employed in SPR imaging measurements of (i) DNA-DNA hybridization adsorption, (ii) DNA-protein bioaffinity adsorption and (iii) the hybridization adsorption of DNA-modified gold nanoparticles onto DNA-functionalized PDA nanorings.

1. Fabrication of DNA Microarrays on Polydopamine-Modified Gold Thin Films for SPR Imaging Measurements


*Langmuir* 2013 29(34), 10868-10873

2. Electrodeposition of Polydopamine Thin Films for DNA Patterning and Microarrays


Analytical Chemistry 2013 85(21), 9991-9995

COLL 284

Hybrid gadolinium metal organic–framework/gold nanoparticles as contrast agents for bimodal imaging

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Imaging contrast agents for magnetic resonance imaging (MRI) and computed tomography (CT) have addressed great attention for early-stage cancer diagnosis. Gadolinium (Gd) metal organic framework (MOF) with tunable size, high Gd3+ loading and multivalency can potentially overcome the limitations of clinically utilized Gd chelcated contrast agents. In this work, we synthesized hybrid GdMOF/Au hybrid nanoparticles through two different approaches: polymer bridged GdMOF/Au and Au/GdMOF core–shell. The resulted nanocomposites, presenting both excellent MRI and CT responses, show potential application as a bimodal imaging contrast agent.
Surface photochemistry of adsorbed nitrate on oxide and zeolite surfaces

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In the atmosphere, nitric acid, nitrogen pentoxide and nitrogen dioxide react with mineral dust particle surfaces to form adsorbed nitrate. This process is thought to be a sink for nitrogen oxides but in fact there is the potential to release gas-phase nitrogen oxides back into the atmosphere due to surface photochemistry of adsorbed nitrate initiated by solar light. In this study, the wavelength dependence of nitrate ion photochemistry when adsorbed onto model laboratory proxies of mineral dust aerosol including Al₂O₃, TiO₂ and NaY Zeolite was investigated using FTIR spectroscopy. These proxies are used to represent non-photoactive oxides, photoactive semiconductor oxides and aluminosilicate materials, respectively, present in mineral dust. Nitrate photochemistry on these materials is shown to depend on the wavelength of light, physicochemical properties of the dust particles and the adsorption mode of the nitrate ion. As will be shown, nitrate ions adsorbed on oxide particles undergo photochemistry over a broader wavelength region of solar spectrum compared to nitrate ion in solution. Gas-phase NO₂ is the major photolysis product under dry conditions. Nitrate photochemistry is more efficient on TiO₂ compared to Al₂O₃ as expected because of its semiconductor properties. Nitrite ion complexed to Na⁺ sites is the major photolysis product found in nitrate photochemistry in NaY zeolite. The wavelength dependence of nitrate photochemistry and proposed mechanisms for the formation of photoproducts are presented.

Photochemical degradation of a brominated flame retardant (tetrabromobisphenol A) in ice under field and laboratory conditions

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Studies of brominated flame retardants have raised awareness of their potential environmental impact as toxic compounds. Because these compounds are now globally distributed, including in the Polar Regions, it is important to assess their potential fate in the environment. It has been shown that active photochemistry occurs in sunlit snow and ice, but there is little information regarding potential photochemical degradation of brominated flame retardants in snow and ice. We have conducted field-based experiments in Barrow, Alaska to investigate the potential photochemical degradation of TBBPA in snow and ice under environmentally-relevant conditions. Field-based results show that TBBPA is efficiently degraded under direct photolysis conditions in frozen aqueous samples under natural Barrow sunlight. In aqueous solution the light absorption properties of TBBPA are pH dependent. Therefore, the photodegradation of
TBBPA in snow and ice will be highly pH dependent. Reactions that are pH dependent may be affected by the nature of the liquid-like layers in snow/ice as well as the presence of other solutes that may indirectly affect the local pH experienced by TBBPA in snow and ice samples. In order to establish how the effective pH of liquid-like regions in ice might impact the degradation of TBBPA, various salts were added to aqueous solutions of TBBPA. Upon freezing, these different salts will induce pH differences in the liquid-like regions of the sample due to a phenomenon known as the freezing potential. Observed reactivity differences upon addition of these salts will be discussed. Additionally, the presence of dissolved organic matter (DOM), an effective environmentally-relevant photosensitizer, has the potential to cause indirect photochemical degradation of TBBPA and this degradation pathway was also evaluated under laboratory conditions.

COLL 287

Characterization of organic matter in ice cores from North America, Greenland, and Antarctica using ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry

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Historically, it has been an analytical challenge to detect and identify the organic components present in ice cores, due to the low abundance of organic carbon. In order to detect and characterize the small amounts of organic matter in ice cores, advanced analytical instrumentation is required. Here we utilize ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), coupled with electrospray ionization, to identify the molecular formulas and compound classes of organic matter in both modern and ancient ice core and glacial samples from Wyoming, Greenland, and Antarctica. A suite of 21 ice core samples were analyzed and thousands of distinct molecular species were identified in each sample, providing clues to the nature and sources of organic matter in these regions. An additional suite of surface snow samples from Barrow, Alaska were analyzed using both FTICR-MS and proton NMR spectroscopy. In all samples, we identify compounds belonging to major biochemical classes, such as lignin, tannins, carbohydrates, proteins, lipids, unsaturated hydrocarbons, and condensed aromatics. The relative abundance of these species vary with age and sample location, and provide clues to the sources and post-depositional processing (e.g., photo-oxidation) of the organic matter. Analysis of the samples shows functional group patterns in modern samples that are indicative of atmospheric processing of organic carbon (e.g., potential sources of organic matter from the deposition of aerosols). Principal component analysis shows that various geographical locations are enriched in different compound classes, indicating potential differences in the major sources of organic matter to these locations. Use of these advanced analytical techniques, capable of characterizing the low concentration organic matter
present at an unprecedented level of detail, now presents us with the opportunity to expand the wealth of knowledge that ice cores could provide for the glaciology, atmospheric, and climate communities.

COLL 288

Investigation of the conversion of nitrogen dioxide to nitrous acid on iron oxide surfaces

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Mineral aerosol represents one of the largest mass fractions of the global aerosols. Iron oxide is a component of mineral dust in the atmosphere that exists in different forms. In addition, these minerals are found in bacteria, insects, weathered soils, clays, rocks, and urban surfaces. We investigated the uptake of nitrogen dioxide onto several different iron oxides as there are both high concentrations of nitrogen dioxide and iron-containing surfaces present in polluted areas. Our data shows that the uptake of nitrogen dioxide on iron oxide surfaces generates nitrous acid, which is an important precursor for hydroxyl radicals in polluted environment. The kinetics of nitrogen dioxide uptake on iron oxide surface was studied using a coated-wall flow tube coupled to a chemical ionization mass spectrometer. Our results show that the uptake kinetics exhibit an inverse dependence on nitrogen dioxide concentration and follows the Langmuir-Hinshelwood mechanism, where reactivity depends on several variables, including the relative humidity of the carrier gas and the type of iron oxide mineral acting as the substrate. The mechanism of HONO formation on these surfaces are discussed along with their implications for atmospheric chemistry.

COLL 289

Chemical imaging analysis of anthropogenic- and biogenic-influenced aerosol particles during the SOAS field campaign

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During the summer, the southeastern United States experiences a cooling haze due to the interaction of anthropogenic and biogenic aerosol sources. An objective of the summer 2013 Southern Oxidant and Aerosol Study (SOAS) was to improve our understanding of how trace gases and aerosols are contributing to this relative cooling through light scattering and absorption. Our measurements focus on single particle analysis of aerosols collected at the Centreville, Alabama SEARCH site. Particles were characterized using an array of chemical imaging techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and Raman microspectroscopy. Through physicochemical characterization methods, sea spray and secondary organic aerosol-containing particles were found to be common types. These analyses provide detailed information on particle size, morphology, elemental composition, and functional groups. The improved understanding will be used to explore how sources and atmospheric processing change particle structure, and how the altered optical properties impact air quality and climate on a regional scale.

**COLL 290**

**Nitrous acid and nitrogen dioxide from nitrate photochemistry in aqueous solutions**

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Nitrate is an abundant component of aerosols, the thin aqueous films coating boundary layer surfaces, and in surface water. Nitrate photolysis generates gas phase nitrogen dioxide and nitrous acid, both of which contribute to tropospheric ozone production. It is understood that when exposed to actinic irradiation, nitrate will photolyze via two pathways, one which generates nitrogen dioxide, and the other nitrite. In this presentation, we will describe results of experiments that used cavity enhanced absorption spectroscopy to simultaneously measure gas phase nitrogen dioxide and nitrous acid evolved during the photolysis of sodium nitrate dissolved in aqueous solution as a function of several critical environmental variables. These laboratory results reveal important insights into the photochemical mechanisms for the formation of nitrous acid in the lower atmosphere.

**COLL 291**

**Complexes leading to particle formation from methanesulfonic acid, amines, and water**

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To complement laboratory studies of new particle formation from methanesulfonic acid (MSA), amines and water, quantum chemical calculations were carried out to determine the structure and stability of initial complexes. MSA, an oxidation product of organosulfur species, does not lead to significant particle formation with water alone. However, MSA could lead to significant particle formation in the atmosphere in the presence of amines and water. Variation in the observed particle concentrations with the precursor amine and the dependence on relative humidity may be related to the calculated structure and stability of the initial complexes.

**COLL 292**

**Development of environmentally friendly CO₂ scrubbers from vegetable proteins**

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Global warming resulted from the emission of greenhouse gases has become an urgent global issue. The burning of the diminishing fossil fuel reserves is accompanied by large anthropogenic CO₂ release, which has outpaced nature's CO₂ recycling capability, causing significant environmental harm. Development of technologies that can reduce and remove CO₂ release is essential to cope with the global demand of CO₂ reduction. Soybean proteins are a by-product of production of soy oil, containing amino and amide (peptide) groups that can interact with CO₂. Among the soybean proteins, glycinin and β-conglycinin are the most important and popular ones possessing β-sheet structures, making them as preferred proteins to capture CO₂ by physical adsorption. In addition, 15% of soybean proteins are made of amino acids containing additional amino groups in side chains such as arginine, lysine and histidine. In this study we have tried to develop a novel technology that can convert soybean proteins into highly porous materials which can serve as efficient absorbents/adsorbents of CO₂. Soy protein isolates were tested in different organic and inorganic solvent systems developed in this group, which can produce proteins in gel forms in higher protein concentrations. Freeze drying process was conducted in order to form the porous solid nitrogen reached structure. These porous structures can ensure hybrid physical and chemical CO₂ capture due to the physical entrapment of CO₂ by the highly porous structure and chemically bonded CO₂ to amino reached structure. To enhance chemical absorption, hydrolyzed soybean protein was mixed with soybean protein isolate in order to have more amino groups within the porous absorbent. The absorption/desorption results show that porous protein based structures have this ability to capture and release CO₂ in an efficient and controlled way.
Fenton oxidation of gaseous isoprene on aqueous aerosol surfaces

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We report that gas-phase isoprene ISO(g) is oxidized upon impacting the surface of aqueous FeCl₂ solutions simultaneously exposed to H₂O₂(g). Experiments involve exposing microjets of micromolar FeCl₂ solutions at pH < 4 to ISO(g) + H₂O₂(g) mixtures for ~ 10 microseconds within the spraying chamber of an electrospray ionization mass spectrometer (ESI-MS). Products are analyzed online in the positive and negative ion modes. We detect protonated monomer and oligomer species (ISO)₁₋₈H⁺, in accord with our previous report (J. Phys. Chem. A, 116 2012 6027), plus myriad (m/z) > 150 oxidation products whose combined yields amount to ~ 5% of (ISO)₁₋₈H⁺. MS/MS analysis reveals that positive ions typically split H₂O and O neutrals, whereas the less abundant negative ions undergo CO, H₂O and CO₂ losses. All products are inhibited by the addition of excess t-butanol to FeCl₂ solutions as ·OH scavenger. These results implicate an oxidation process initiated by the addition of interfacial OH and/or HO₂ to ISO leading to poly-alcohols, carbonyls, hydroperoxides and carboxylic acids. We infer that gaseous olefins can be oxidized upon impacting the surface of Fe-containing aqueous environmental surfaces, including those of aerosols.

COLL 294

Polymer cages for size selective fishing of colloidal metal nanoparticles

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Based on the concept of mono-functionalization of gold nanoparticle (AuNP) using surface polymerization, novel hybrid materials of precisely controlled artificial molecules with functionalized polymer have been designed.
The polymeric ligand sphere on AuNP surface was used as a universal synthetic tool for precious metal nanoparticles. After etching gold cores, the polymer nanoparticle-cages were refilled with Ag-, Pd- and Pt-nanoparticles by in-situ reduction route. The cages, so-called “fish nets”, were also used for size-controlled separation of colloidal AuNPs.

Citrate stabilized AuNPs (Ct@AuNP) in different sizes were used as “fish”. The cages captured AuNPs under 15 nm in diameter with high efficiency. When a mixture of Ct@AuNP in different sizes was used as “fish”, the cages caught more small AuNPs (3 nm) than large AuNPs (15 nm) and the oversize “fish” was excluded. This concept will
open new perspectives for one-step preparation of various hybrid materials with size-controlled nanoparticles for different applications.

COLL 295

Assembly and disassembly of calixarene-based amphiphiles controlled by molecular recognition

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Amphiphiles are able to self-assemble into various nanoscale multimolecular assemblies ranging from simple micelles and vesicles to highly organized fibers, helices and tubes. Amphiphilic assembly has gained more and more attention in chemistry, biology, as well as environmental science. Compared with conventional amphiphiles, macrocycle-based amphiphiles have attracted much attention due to their distinctive aggregation behavior. Owing to the reorganized conformation, calixarene-based amphiphiles present a higher tendency to form micelles. However, the molecular recognition of calixarene cavity has almost been ignored to manipulate the assembling behavior of calixarene-based amphiphiles. Herein, we describe a host-guest approach to regulate the assembly of calixarene-based amphiphiles reversibly in virtue of the cavity binding.

Scheme 1. Principle of controlled disassembly and reassembly of calixarene-based amphiphile.
We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

References


**COLL 296**

**Highly efficient nanosubstrate-mediated delivery of gene-encapsulated nanoparticles based on molecular recognition**

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In the presentation, I will introduce a new gene delivery system, NanoSubstrate-Mediated Delivery (NSMD) platform, based on two functional components, including 1) DNAISNPs: supramolecular nanoparticle (SNP) vectors for encapsulation of gene, and 2) Ad-SiNWS: adamantane (Ad)-grafted silicon nanowire substrates. The multivalent molecular recognition between the Ad motifs on Ad-SiNWS and the β-cyclodextrin (CD) motifs on DNAISNPs leads to dynamic assembly and local enrichment of DNAISNPs from the surrounding medium onto Ad-SiNWS. The topographic interactions between SINWS and cells result in a highly efficient delivery of exogenous genes. In addition, NSMD system enables continuous and multi-round delivery of the gene using the same substrates without depositing payloads and immobilizing cells in each round of delivery. Using the NSMD platform in vivo, cells recruited on subcutaneously transplanted Ad-SiNWS were also efficiently transfected with exogenous genes loaded into SNPs, validating the in vivo feasibility of this system.

**COLL 297**

**Disulfide-containing supramolecular nanoparticles for targeted drug delivery**
Although researchers reach a consensus that some hydrophobic drugs or bioactive molecules may have great therapeutic impacts, the specific delivery of these molecules to the disease-associated target sites is still a primary roadblock for the clinical formulation of drug compounds into truly potent medicines. Therefore, the design of adequately tailored delivery methodology is of prime importance. Herein, we would like to report a novel adamantane-modified hyaluronic acid (HA-ADA) capable of effectively binding disulfide-containing bridged bis(β-cyclodextrin)s (1) through the noncovalent multiple interactions. The combination of hyaluronic acid polymers with disulfide linkages not only endows the resultant nanoparticles with targeting and redox properties, but also offers a hydrophobic microenvironment to entrap the anti-cancer drug of paclitaxel (PTX) under physiological condition. The assembling behaviors and drug loading efficiency were investigated by spectroscopic titrations and microscopic experiments. In our case, the morphological size of supramolecular architectures could be efficiently modulated by the redox-controllable cross-linker.

Scheme 1. Construction of nanoparticles and TEM (a, c) and AFM (b, d) images of HA-ADA in the absence (a, b) and presence (c, d) of 1

We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

References:
Hyaluronic acid-conjugated graphene nanosupramolecular assembly for drug targeting and controlled release

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Due to its extraordinary physical and chemical properties, graphene and its derivatives have made great development in the field of biomedicine research. The construction of safe and efficient nano-graphene drug carries is still a hot topic. Herein, we would like to report a nanosupramolecular assembly (GO-CD-HA) which is fabricated through the noncovalent multiple interactions between the $\beta$-cyclodextrin-modified graphene oxide (GO-CD) and adamantane-bearing hyaluronic acid (HA-ADA). Compared with GO-CD, GO-CD-HA nanosupramolecular assembly showed increased solubility and stability under physiological environment. The size distribution of GO-CD-HA is 50~150 nm. Significantly, camptothecin (CPT), a water-insoluble anticancer drug, can be loaded onto GO-CD-HA through $\pi-\pi$ stacking and hydrophobic interaction, and then continuously released in vitro.
Figure 1. Construction of GO-CD-HA-CPT conjugates, AFM images (a, b) and UV/vis spectra (c) of GO-CD-HA and GO-CD-HA-CPT, and fluorescence spectra (d) of CPT and GO-CD-HA-CPT.

We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

References


 COLL  299

Electro-responsive supramolecular polymeric hydrogel

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Hydrogels have highly variable mechanical properties, making them increasingly important in a variety of biomedical and industrial applications. Supramolecular polymeric hydrogels are three-dimensional networked materials that specific and dynamic non-covalent interactions are used as the structural crosslinks. As one kind of widely studied non-covalent interactions, macrocyclic host–guest complexation has been engaged in supramolecular cross-linking, and further fabricating hydrogels. p-Sulfonatocalixarenes represent a family of water-soluble macrocycles, and show strong binding affinity and high molecular selectivity towards organic cations, driven by the synergistic effect of additional anchoring points donated by sulfonate groups together with the intrinsic cavities. Notably, hydrogels driven by molecular recognition of p-sulfonatocalixarenes are barely reported. Herein, we wish to report a supramolecular hydrogel based on the host-guest complexation of p-sulfonatocalix[4]arene tetradecl ether with viologen-grafted polymer. p-Sulfonatocalixarenes adorned at the lower rim with alkyl chains can form micelles with special recognition site (calixarene cavity) on its out-layer surface, which could be further hierarchically assembled. The micelles were then cross-linked by the viologen-grafted polymer, generating the three-dimensional network. As viologen is redox-active, the obtained supramolecular hydrogel is responsive to electro-stimulus.
Scheme 1. Formation of the supramolecular hydrogel by cross-linking of the polymer chains via host-guest inclusion complexation of the viologen substituents and the macrocyclic hosts on the surface of $p$-sulfonatocalixarene micelles.

We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

References


COLL 300

Multifunctional lipid vesicles embedded with amphiphilic calixarenes

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The development of multifunctional nanocontainers for imaging, targeting, and drug release is of great importance. Herein, we fabricated multifunctional lipid vesicles with amphiphilic $p$-sulfonatocalixarenes. Liposomes are the leading drug delivery systems for the systemic (intravenous) administration of drugs and calixarenes are embedded in the bilayer since their amphiphilic nature. The resulting functionalized lipid vesicles exhibited requisite characteristics for drug delivery purposes: (i) a negative charged outer shell resulting from $p$-sulfonatocalixarenes which leaded to colloidal stabilization, (ii) facile, non-destructive, noncovalent, and modular surface modification using specific host–guest chemistry, (iii) fluorescent properties provided by the non-covalent linkage of a FITC-based dye to the surface, and (iv) surface functionalization with biologically active ligands that enabled specific targeting. The functionalized lipid vesicles could be internalized into targeted cells (MCF7) by receptor-mediated endocytosis. This assembling strategy can be extended to design smart multifunctional materials for biomedical applications.

**Scheme 1.** Schematic illustration of lipid vesicles embedded with amphiphilic calixarenes.

We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

**References:**

Design of patchy polymersomes with topological surface patterns at the nanoscale

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In Nature, biological membranes are composed of several components, which have been found to display nanometer and micrometer surface domains, called “rafts”. Such domains play an important role in many biological processes such as cellular signaling, membrane trafficking and membrane modeling.

Our research focuses on the design of these complex artificial systems using synthetic membrane forming diblock copolymers as main constituents. These polymeric systems, a.k.a. polymersomes have recently yielded vesicles with patterned surfaces, using binary mixtures of diblock copolymers. Their surface topology could be controlled by the molar ratio of both block copolymer chains as well as their molecular weight. However, it was observed that such systems evolve upon ageing towards asymmetric polymersomes, where phase segregation of diblock copolymers occurred.

To slow down this phenomenon, we propose to combine a diblock copolymer AB and a triblock copolymer ABC to prepare patchy polymersomes. In that case, the triblock copolymer would stabilize the patterns within the membrane, thus acting as a lineactant (Figure 1a). To validate this concept, series of polymersomes made of AB and ABC block copolymers were prepared and characterized using TEM, DLS and cryo-TEM. Systematic analysis using FFT filtering was performed on the images to estimate the size of patterns. From these experiments, we observed the formation of patterns within polymersome membrane (Figure 1b and 1c), whose size varies as a function of copolymer mixture composition. In addition, these patterns were shown to be stable over 1 month, thus validating our concept.


COLL 302

Host-guest nanomaterials: A comparison of Brooker's merocyanine interactions with modified β-cyclodextrins

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Cyclodextrin molecules have been used to create unique nanomaterials for a variety of applications, but there is much to learn about the behavior of guest molecules found within the cavity. The binding and overall stability of the guest molecule must be well-characterized in order to optimize these materials for use in practical supramolecular chemical systems. Brooker's merocyanine (4-[(1-methyl-4(1H)-pyridinylidene)ethylidene]-2,5-cyclohexadien-1-one) has an interesting protolytic/photolytic isomerization cycle that was found to be affected by encapsulation within the β-cyclodextrin cavity. The focus of this study was to understand this isomerization behavior within a series of modified cyclodextrins and to characterize the
binding efficiency and thermodynamics of complex formation of these systems using UV/Vis and fluorescence spectroscopy. Modifications included different degrees of substitution at the primary and secondary rims of the cyclodextrin cavity with hydroxyethyl, hydroxypropyl, methyl, or sulfate substituents in order to compare the effect of hydrogen bonding, ionic interactions and steric effects on the host-guest structure. Results indicated that the largest effect on the complex behavior was from the ionic charges and/or steric effects of the sulfate group, while the various hydrocarbon modifications had a smaller effect on binding. In all cases, however, the formation of the complex was hindered as substituents were added to the cyclodextrin. Computational modeling was also used to compare the resulting host-guest structures at the molecular level to determine where Brooker's merocyanine was located within the cavity in order to rationalize the isomerization behavior. An understanding of the behavior of Brooker's merocyanine with a variety of cyclodextrin molecules can then be applied to other related guest molecules that must remain stable when used in host-guest applications such as in drug delivery nanomaterials, and an increase in the fundamental knowledge of these materials can be achieved.

COLL 303

Comparing and correlating solubility parameters governing self-assembly of molecular gels

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Solvent properties play a central role in mediating the aggregation and self-assembly of molecular gelators and their growth into fibers. Numerous attempts have been made to correlate solubility parameters of solvents and gelation abilities of molecular gelators, but a comprehensive comparison of the most important parameters has yet to appear. Here, the degree to which partition coefficients ($logP$), Henry's law constants ($HLC$), dipole moments, static relative permittivities ($\varepsilon_r$), solvatochromic $E_T(30)$ parameters, Kamlet-Taft parameters ($b$, $a$, and $p$), Catalan's solvatochromic parameters ($SPP$, $SB$ and $SA$), Hildebrand solubility parameters ($d_l$), and Hansen solubility parameters ($dp$, $dd$, $dh$) and the associated Hansen distance ($R_{ij}$) of different solvents (covering a wide range of properties) can be correlated. The approach describes the basis for each of the parameters and how it can be applied. As such, it is an instructional 'blueprint' for how to assess the appropriate type of solvent parameter for use with molecular gelators as well as with molecules forming other types of self-assembled materials. The results reveal several important insights into the factors favoring gelation of solvents. The ability of a solvent to accept or donate a hydrogen bond is much more important than solvent polarity in determining whether mixtures become solutions, clear gels, or opaque gels. Thermodynamically derived parameters could not be correlated to the physical properties of the molecular gels unless they were dissected into their individual HSPs. It is also found that the fate of the molecular gelator, unlike that of polymers, is influenced not only by the magnitude of the distance between the HSPs for the gelator and the HSPs of the solvent, $R_{ij}$, but also by the directionality of $R_{ij}$.
Strong carbon dative bond formed by isocyanides on the Ge(100)-2 × 1 surface

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Functionalization of semiconductor surfaces with organic molecules has been of much interest in recent years. For example, adsorbates that donate or withdraw electron density can be useful for modification of the band structure of semiconductor surfaces. To this end, isocyanides are potentially interesting adsorbates because at metal surfaces, σ-bonded isocyanides are known to form highly conductive molecular junctions. However, there have only been a few studies of isocyanide adsorption on semiconductor surfaces. In this work, we report the dative bond formation of tert-butyl isocyanide on a single crystalline germanium surface, providing the first experimental demonstration of a dative bond through the carbon atom at a semiconductor surface. The nature of the surface-adsorbate bond was determined with infrared spectroscopy experiments and density functional theory calculations. The dative-bonded adsorbate is characterized by an N≡C stretching frequency significantly blue-shifted from that of the free molecule. Moreover, the adsorbate N≡C vibrational frequency red-shifts back toward that of the free molecule upon increasing coverage. These spectroscopic effects are attributed to σ-donation of the isocyanide lone pair electrons. Moreover, from temperature programmed desorption, an adsorption energy greater than 25 kcal/mol was found, which is the highest reported to date of any organic molecule dative bonded to this surface. This study therefore provides important evidence for strong dative bond formation at a group 14 semiconductor surface, which has implications for future organic-inorganic hybrid electronics.

Photocatalytic degradation of contaminants by colloidal AgCl(s): Kinetic and mechanistic insights

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Silver halide and associated assemblages have received a great deal of interest in recent years for their ability to photochemically degrade a wide variety of substrates. In this work we examine the reactivity of an in-situ formed silver chloride colloid to degrade rhodamine B dye (RhB) - considered here as a model substrate. The AgCl(s) particles thus produced had hydrodynamic diameters between 0.2 - 1 µm and exhibited differing degradation potential as the concentrations of silver, chloride and pH were varied. Using a spectral deconvolution procedure, RhB was shown to be degraded both by de-ethylation and by destruction of the chromophore, with only minimal build-up of
intermediate degradation products prior to chromophore destruction under most conditions.

Complementary studies examining the production of hypochlorous acid (HOCl) in this system (in the absence of RhB) have also been performed and the reaction of RhB and HOCl examined. The reaction of RhB with HOCl led to the formation of chlorinated RhB species, which were not observed during photochemical reactions with AgCl(s). These results indicate that the hole-electron pairs formed in the primary photochemical process drive the oxidation of chloride ions to chlorine atoms, subsequently leading to HOCl production. However, in the presence of an oxidisable substrate, this reaction profile is apparently blocked, suggesting a competitive mechanism between RhB and chloride ion for oxidation, and the direct oxidation of RhB by photo-generated holes.

The presence of oxygen facilitated the process greatly, with removal of oxygen considerably slowing the RhB photodegradation. This result suggests that oxygen was an effective sink for photo-formed electrons in the conduction band of AgCl(s), thereby enhancing hole-electron pair separation. Hydroxyl radical and hydrogen peroxide are also shown not to be implicated in RhB degradation.

**COLL 306**

**Near ambient pressure X-ray photoelectron spectroscopy study of dissociative adsorption of water on GaAs surface**

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The ubiquitous presence of water in ambient air and solutions results in the coverage of device surfaces by layers of water in practical applications. Resolving the electronic structure and chemistry at the water/semiconductor interface have always been a central issue in material science and still remains challenging. Due to the complicated chemical environment in device applications, study of water adsorption and chemical behavior under operando conditions at the H₂O/semiconductor interface are especially important.

In the present work, dissociative adsorption of water on GaAs surface is investigated using X-ray Photoelectron Spectroscopy (XPS) performed in-situ under near realistic conditions. Enhanced surface Ga oxygenation and hydroxylation are observed when the GaAs surface is exposed to elevated pressures of water vapor (from UHV to 5 mbar). The evolution of water dissociative adsorption is reflected by the shape and position changes in the photoemission spectra of Ga 2p, As 2p and O 1s. On the other hand, increased temperature (from RT to 773 K) leads to more vigorous surface Ga oxidation and hydroxylation, as well as the quick desorption of weakly adsorbed water molecules.
and/or their dissociation products. The chemistry process at the H₂O/GaAs interface is summarized in the following figure.

Spatially localizing ligands on single CdSe/CdS seeded nanorods

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Super-resolution techniques that allow the spatial localization of labeled probes at the single molecule level are used to investigate individual ligand binding events on nanorods. This single molecule based technique aims to spatially resolve ligands on nanorod surfaces to reveal the distribution of active or defect sites on a nanorod. Such knowledge will advance the use of nanorods in separation membranes or as light harvesters in solar fuel applications. Using total internal reflection fluorescence microscopy, cadmium sulfide nanorods with cadmium selenide seeds, and labeled ligands consisting of boron-dipyrrromethene dyes are studied. Spatial localization is possible because both nanocrystal and dye have superior photochemical stability and quantum yields, while their emission is designed to have negligible overlap. The precise counting of dye molecules on a single nanoparticle is enabled by the stochastic photobleaching of dyes with binary on-off emission states. Our studies reveal that ligands with a more nucleophilic binding group bind more strongly and in greater quantity, while longer rods (>300 nm) have more binding sites than shorter rods (< 80 nm).

Interestingly, in our experiment, the proportion of nanorods that resist ligand exchange
are revealed. Our single particle studies reveal the static and dynamic heterogeneity inherent in nanoparticle samples.

**COLL 308**

**Characterizing the activity and stability of enzymes immobilized on maleimide-functionalized PEG monolayers**

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Because of their ability to catalyze complex chemical reactions under mild reaction conditions, enzymes are increasingly being used for a variety of applications, ranging from industrial catalysis to biosensors and tissue engineering. To facilitate reuse, enzymes are often tethered to a variety of surfaces. While others have shown that immobilization increases the stability of an enzyme, the activity often decreases. The molecular mechanisms involved are poorly understood. A number of variables may explain this drop, including unfavorable orientation, protein unfolding, and restricted protein dynamics. To explore this question, we are using 6-phospho-β-galactosidase from *L. lactis* (PDB: 2PBG) as a model enzyme. This enzyme is tethered to a maleimide-functionalized PEG monolayer via a unique surface cysteine engineered into the protein. By altering the location of the cysteine, we can alter the orientation of the enzyme active site and the protein attachment point. We have been able to show that an oriented enzyme has much greater activity than one that is randomly adsorbed to the surface. In addition, we have shown that attaching the protein to the surface at different secondary structures on the protein can affect the thermal stability. In the future, we will expand this research to examine multiple tethering sites, and surface crowding will have on enzyme activity.

**COLL 309**

**Raman spectroscopy of interfacial chemistry between sexithiophene and vapor-deposited low work function metals**

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Thiophene-based conjugated polymers are widely applied in organic photoelectronic devices due to their unique optical and electronic properties. Recent research on oligothiophenes as simple models of polythiophenes has demonstrated molecular structural changes from intramolecular torsion along the oligothiophene chain or reaction chemistry that can drastically affect the pi-conjugated electron delocalization along the molecular backbone. Such changes result in a reduction of the effective conjugation length of the oligothiophene, and hence, its conductivity. In this work, sexithiophene (6T) thin film models are subjected to vapor deposition of thin layers of Ag, Al, Mg and Ca, common cathode contact materials, and the resulting interfacial
chemistry monitored with surface Raman spectroscopy in ultrahigh vacuum. Metal atoms are estimated to penetrate the 6T films to depths of 2.5 - 5 nm, although interfacial structural changes are induced only by the first 0.5 nm of deposited metal. Intramolecular torsion along individual 6T chains is observed when the contact material is Ag, Al or Mg, causing a change in 6T effective conjugation length. In contrast, reaction chemistry occurs with Ca resulting in the formation of small but observable amounts of amorphous carbon.

COLL 310

Synthesis and characterization of uniform multicomponent \((\text{BaSrMg})\O\) oxygen-selective sorbent for \(\text{O}_2\) separation

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The technology of oxy-fuel combustion with pure oxygen or enriched air instead of air plays an important role in the combustion of fossil fuel. Among oxygen-selective materials, the high capacity and selectivity of BaO is very attractive in oxygen separation, if the thermal properties and oxygen partial pressure in the transition of BaO redox reaction are improved. Here, we synthesized uniform multi-component \((\text{BaSrMg})\O\) particles with great improvement in oxygen separation by a facile method, in which the \((\text{BaSrMg})\O\)particle was converted from \((\text{BaSrMg})\text{CO}_3\) particle. Firstly, the homogeneous \((\text{BaSrMg})\text{CO}_3\) particles composed of 52 % (Ba), 6% (Sr), 42 % (Mg) were synthesized. On continuous reduction of \((\text{BaSrMg})\text{CO}_3\) particles under \text{H}_2\ environment, the porous \((\text{Ba}_0.52\text{Sr}_0.06\text{Mg}_0.42)\O\) particles used for \text{O}_2\ separation were prepared. The porous \((\text{Ba}_0.52\text{Sr}_0.06\text{Mg}_0.42)\O\) particles perform a high \text{O}_2\ capacity (2.02 mmol/g) at 700 °C owning to the high content and selectivity of BaO in the particle, as well as behave good thermal stability because of the robust MgO well distributing in the crystal to prevent sintering of BaO\(_2\) at high temperature. In particular, due to the incorporation of strontium in the \((\text{BaSrMg})\O\) crystal lattice, the oxygen partial pressure for the transition of BaO redox reaction enhance from less than 10 % to 19.47 %, which would reduce the energy cost in the release of pure oxygen. However, because the composition of Sr in the \((\text{Ba}_0.52\text{Sr}_0.06\text{Mg}_0.42)\O\) particles is unchangeable, which limited to further increase oxygen partial pressure for \((\text{BaSrMg})\O\) redox reaction, the \((\text{BaSrMg})\O\) particles with controllable composition were synthesized based on the various precursor, \((\text{BaSrMg})\text{CO}_3\) microsphere. The porous \((\text{BaSrMg})\O\) microspheres with high content of strontium show a sharp improvement of oxygen partial pressure in transition of BaO redox reaction. The porous \((\text{BaSrMg})\O\) particle as an oxygen-selective sorbent is a significant breakthrough in the development of oxygen separation or enrichment.
COLL 311

Quantifying the initial carboxylic acid ligand exchange events on CdS nanocrystals

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An understanding of the nanocrystal-ligand interface is paramount for any optoelectronic devices or biological labels based on these materials. Here, we quantitatively study the initial binding events on 5.0 nm oleic-acid capped CdS nanocrystals (NC). This is done by correlating the change in CdS Photoluminescence (PL), which is due to fluorescence resonance energy transfer (FRET) from the CdS donor to an acceptor, a specially designed dye functionalized with a carboxylic group. This work first reveals the initial binding events between cadmium chalcogenide NCs and carboxylic acid groups. Until now, quantitative study at such low concentrations has been hindered by the high concentration required by NMR, and the spectroscopically silent nature of the carboxylic acid group in photoluminescence-based studies. A good fit was obtained from our model for both the experimental steady-state and time-resolved photoluminescence data by assuming a Poissonian binding distribution. A modified Langmuir isotherm involving a ligand with one binding group to identical, multiple binding sites on the surface of CdS NC can describe the binding behavior well. Specifically, there are an average of 3 new carboxylic acid ligands on the CdS surface with a binding constant, $K_a$, of $4.7 \times 10^5$ M$^{-1}$

COLL 312

Understanding the crystal growth inhibition: Role of acetate at the calcium oxalate/water interfaces

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Calcium oxalate occurs widely in kidney stones and among a variety of living organisms[1]. The presence of bio-polymers such as polyacrylate, polyaspartate or polyglutamate during the formation of calcium oxalate crystal has a great impact on the crystalline phase, morphology and growth rate[2-4]. In spite of advances in the experimental characterization of the influence that these bio-polymers exert on the crystallization of calcium rich biominerals, a full understanding of these processes on a molecular scale has not yet been accomplished. First principle molecular dynamics simulations offer a valuable tool to complement experimental investigations, thanks to the possibility to accurately describe the heterogeneous environment at interfaces, where polarization effects and specific hydrogen bond dynamics play a key role. We provide here a structural and dynamical characterization of the interfaces between calcium oxalate dihydrate(COD) (100) and (101) and water, which reveals differences in
the structure of interfacial water and in the local coordination of calcium ions on the
surface. Moreover we characterize the interaction between different surfaces of COD
and biomolecules. As a first step we consider acetate as an analogue for the
carboxylate group of glutamate side chains, and we estimate its binding structure and
free energies on different COD surfaces at different coverage. Preferential binding of
carboxylate to the (100) surface is found, providing a rational for recent experimental
results on anisotropic growth of COD crystals in the presence of biopolymers[2]. These
results also serve us to calibrate empirical models to study polymer-controlled crystal
growth of calcium oxalate in large scale atomistic simulations.


**COLL 313**

**Optical properties of gold nanorattles: Evidences for free movement of the inside solid nanosphere**

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Gold nanorattles (AuNRTs), hollow gold nanospheres with internal small solid gold
nanospheres (AuNSs), were prepared with different sizes. The presence of AuNS inside
the hollow gold nanospheres in the nanorattle shape was found to improve their sensing
efficiency. The sensitivity factor of the nanorattles is in the range of 450 nm/RIU, while
the individual hollow nanosphere's efficiency is \( \sim 300 \) nm/RIU. This improvement is due
to the strong plasmon field on the cavity and around the inner gold nanosphere as
shown by using the discrete dipole approximation (DDA) calculations. Interestingly, this
nanoparticle produces a strong enhancement for the interaction of light at 850 nm due
to the excitation of both the inner sphere and outer nanoshell, despite being the fact that
NIR radiation (850 nm) has very low energy to excite the inner gold nanosphere when
present alone. Comparing the experimental and simulated scattering spectrum for a
single colloidal nanorattle suggests that the interior gold nanosphere moves freely
inside the gold nanoshell. When the rattle is dried, the nanosphere adheres to the inner
surface as shown from the experimental and theoretical results. Unlike nanospheres
and nanoshells, the nanorattles have three plasmon peaks in addition to a shoulder.
This allows the AuNRTs to be useful in applications in the visible and near IR spectral
regions.
Effect of strain on ligand binding to Cadmium chalcogenide nanocrystals

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Scaling laws at the nanoscale differ from the bulk due to reasons ranging from the high surface energy of nanoparticles (NPs) to quantum confinement. Here we study core-shell NPs because the strain in their shell varies as a function of shell thickness. Core-shell NPs are unique because their photophysical properties can be tuned based on their composition, size, and shape. Organic ligands serve as a tool for functionalizing these nanoparticles. We seek to determine how the strain in the shell of a Type II core-shell nanostructure affects ligand binding at equilibrium. This is achieved by using a fluorescence resonance energy transfer (FRET) based method for quantifying the initial ligand binding events. As strain increases in the shell, the ligand binding constant is expected to increase. Computationally, the use of density functional theory would provide insight into the orientation of these structures, and the energetics of adsorption and desorption.

Mixed ligand architectures on monolayer protected gold nanoparticles: Analyte-induced assembly and binding interactions

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The interactions of nanoparticles with biomolecules, surfaces, or other nanostructures can be deliberately controlled through appropriate design of the nanoparticle’s surface chemistry. The dimensions, composition, and functionality of the ligand shell define a three-dimensional architecture governing the nanoparticles interactions and can be used to establish a platform that confers desirable physical properties and/or may be further modified. However, difficulties in the synthesis and characterization of monolayer protected nanoparticles have convoluted assessment of the individual roles functional ligand density, mixed ligand structure, and core sizes play in material construction and behavior. This presentation will describe a two-pronged approach involving microfluidic direct synthesis and multiple analytical techniques, including small angle X-ray scattering and NMR characterization, to reproducibly access well-defined mixed monolayer gold nanoparticles (AuNPs) and correlate ligand architecture to material function. This strategy has been employed to design and prepare mixed monolayer architectures to assess how the architecture influences (a) NP-NP assembly that is the critical transformation used to provide an optical readout for biological and chemical sensing approaches and (b) drug-AuNP conjugate formation that can lead to efficient and targeted biological probe materials. We will show how the controlled, reproducible
assembly of AuNPs induced by terminal Ln^{3+}-malonamide binding interactions can be achieved by ligand shell architecture refinement and optimization of malonamide ligand density. The construction of structurally well-defined mixed monolayer protected AuNPs tailored to bind biomarker enzymes and act as targeted X-ray contrast materials for cardiovascular diseases will also be presented.

COLL 316

Role of sulfur-based nanocrystal ligands in metal chalcogenide nanocrystal inks

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Recent discoveries have demonstrated ample opportunities for engineering the surface chemistry of nanocrystals, extending beyond traditional ligands to include small molecules and inorganic compounds. This surface chemistry can be used to control properties including solubility, superlattice spacing, conductivity, electronic structure, and more. Here, we explore the effect of different surface chemistries on the behavior of nanocrystal inks. An ink typically utilizes colloidal suspensions of nanocrystals which, upon annealing, sinter to form larger polycrystalline grains, surrendering their nano-scale properties. Applications encompass sensors, displays, photovoltaics, and other optoelectronic devices. In such systems, a desirable ligand should control surface reactivity between nanocrystals, leave no residue after annealing, and maintain solubility of the ink during film preparation. We employ both inorganic and organic sulfur-based ligands including ammonium sulfide and alkyl thiols the surface of tin sulfide and zinc sulfide nanocrystals and analyze their effect on thin film formation. The efficacy of these ligands is measured in exchange efficiency as well as the morphological, structural, optical, and electronic properties of the resulting thin films. Sulfur-based ligands are shown to enhance the thin film quality including increases in grain size and purer compositions while maintaining optical integrity. We demonstrate a strong correlation between these properties and the surface chemistry employed, and suggest further improvements for nanocrystal inks.

COLL 317

Chemical engineering of oriented attachment of PbSe nanoplates: A theoretical approach for their surface chemistry

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We are investigating the surface chemistry of quantum dots to provide insights into the chemical engineering of self-assembling of PbSe QDs into 1-D and 2-D arrays. Using DFT, we are analyzing the strength of interactions between passivating ligands, such as
chlorides and amines, and different surfaces of the QDs. Different modes of ligand attachments, including ionized (Cl\textsuperscript{-}), radical (Cl\textsuperscript{•}), and salt-like (PbCl\textsubscript{2}) forms, are simulated. The effect of different ligands attachments on the electronic and optical properties of QDs is also studied. We found that Cl and O adsorbed as radicals results in appearing of optically dark trap states in the gap of the QD, when adsorbents are coordinated only with Pb ions. However, when chlorides or oxides are coordinated with both Pb and Se ions on the QD surface, the mid-gap states are eliminated. Cl\textsuperscript{-} ions and PbCl\textsubscript{2} demonstrate preferential binding to the \{110\} surface of the QD, while do not contribute to edge of the valence and conduction band of the QDs. These computational results agree with the experimental observations.

**COLL 318**

**Strong metal-support interaction effect on the catalytic activity of 2D Pt nanoparticle arrays on oxide thin films**

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Catalysis is a critical technology for solving the global challenges of environmental problems and limited energy sources. Especially, Strong metal–support interactions are a key issue in determining the catalytic performance of heterogeneous catalysis. Here, we investigated the support effect in two-dimensional Pt nanocatalysts on reducible metal oxide supports under catalytic reaction. Several reducible metal oxide supports, including CeO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, and TiO\textsubscript{2} thin films, were prepared via the sol-gel process. The Langmuir–Blodgett technique and arc plasma deposition (APD) process were employed to obtain Pt nanoparticle arrays with and without capping layers, respectively, on an oxide substrate. We found that reducible metal oxide supports have a uniform thickness under 50nm and crystalline structure after annealing, and exhibit a bandgap of 3.2–3.8 eV. We tested the catalytic activity of CO oxidation over Pt nanoparticles supported on metal-oxide thin films under 40 torr CO and 100 torr O\textsubscript{2}. Pt catalysts exhibited the better performance on the CeO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2} and SiO\textsubscript{2} in sequence for both the colloidal and APD Pt nanoparticles. These catalytic behavior show a strong support effect on the catalytic performance of two-dimensional Pt nanocatalysts on oxide substrates under CO oxidation, with possible applications of tuning catalytic activity via engineering metal–oxide interfaces.
Cerium oxide (CeO$_2$) nanoparticles are widely used in catalysis. The outstanding catalytic properties of CeO$_2$ are due to its remarkable redox ability, oxygen storage capability, and ionic conductivity. As catalytic processes are usually taking place at the surfaces, the catalytic properties can be further tuned by control of the exposed facets of CeO$_2$ nanoparticles. Although the importance of the atomic structures on different facets is well documented, the atomic surface structures of CeO$_2$ nanoparticles have been uncertain. The underlying problem is the difficulty of direct observation of the O atoms. With aberration-corrected electron microscopy, we were able to i) observe both Ce and O atoms and ii) determine the atomic surface structures of the (100), (110) and (111) facets. The high energy (100) surface contains Ce, O, and reduced CeO terminations simultaneously on the outermost surface as well as the partially occupied lattice sites in the near-surface region (≈1 nm from the surface). The co-existence of multiple surface terminations demonstrates that previous understandings of the (100) surface have been oversimplified. For the (110) surface, there exists a combination of reduced flat CeO$_{2-x}$ surface layers and “sawtooth-like” (111) nanofacets. The CeO$_2$ (111) surface is O-terminated, which is in agreement with electrostatic considerations. Furthermore, the surface structures derived from this microscopy study are consistent with results from our macroscopic infrared spectroscopy investigation. The variation in surface defect density amongst these three facets is responsible for their differences in catalytic activity.
Excess electron trapping at surface oxygen vacancy in TiO2: Origin of STM anomaly

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Owing to its photocatalytic properties and ease of preparation, TiO\textsubscript{2}(110) has been intensively studied as a model surface of metal oxide. While the oxygen vacancies on the TiO\textsubscript{2} surface are known as the active site for catalysis, there is debate on the nature of the excess electrons present due to the oxygen vacancy. The question for the surface reactivity is whether they are localized or delocalized. There has been extensive interest in computational approaches to TiO\textsubscript{2} reactivity. The current view is that excess electrons have localized nature, forming a polaronic Ti\textsuperscript{3+} state and have a stable position at subsurface.[1]

Experimentally, resonant photoelectron diffraction supports this view.[2] However, the results vary among several scanning tunnelling microscopy (STM) experiments. While Minato et al. conclude that excess electrons are delocalized,[3] Papageorgiu et al. conclude that only the -2 charged oxygen vacancy can explain the features observed in STM images.[4] To interpret STM, one needs a high-quality Density Functional Theory (DFT) calculations, which currently are lacking.
We conducted DFT calculations employing hybrid functionals. The results clearly show that localized excess electrons can reproduce the features observed in STM experiments. Typical STM images can be obtained only with the slab larger than 6x2, which amounts to 8.3% oxygen vacancies. Also our calculations highlight the unusual negative charge associated with the oxygen vacancy. In summary, our results not only explain the nature of excess electrons associated with the oxygen vacancies, but also opens a new pathway to characterize defect states at the metal oxide surfaces.


COLL 321

Selective adsorption of ions to aqueous interfaces: Mechanism and effects on evaporation rates

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By exploiting the strong charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their interfacial adsorption properties are measured by UV-SHG spectroscopy. Temperature and concentration dependences are determined, with the goal of establishing a complete molecular description of selective ion adsorption. A study of thiocyanate reveals that its strong adsorption is driven by hydration forces and impeded by a novel entropy effect. A study of nitrite indicates adsorption as an ion pair with sodium. Water evaporation rates are measured by combining liquid microjet technology and Raman thermometry. The relationship between surface propensities of ions and evaporation rates is investigated. A detailed molecular mechanism for both selective ion adsorption and aqueous evaporation is explored.


COLL 322
Wetting of ionic-functionalized surfaces

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Surface wetting can be efficiently tuned by ionic functionalization. Using Molecular Dynamic simulations, we investigate wetting regimes at the nanoscale on molecular-brush coated graphane surfaces. We control hydrophilicity by covering the surface with a mixture of covalently bonded alkyl chains and sporadic ionic groups at varied densities, surface patterns, and electrolyte concentration in the solution. We present a comparison with the effect of uniform electrode charge, advantageous for transient control of pore hydrophilicity, and solution phase behavior inside an apolar confinement. Our findings provide guidance for the design of ionically nanopatterned materials with tailored hydrophilicity at preserved material structure and minimal chemical modification.

COLL 323

Hydration mimicry: A strategy for fast ion transport through membrane nanopores?

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Fast transport of dissolved ions and molecules from one solution to another is important for many chemical and biological processes. An example is transport of ions across synthetic membranes for efficient water purification or osmotic power generation. Another example is ion transport across cellular membranes for electrical signaling. A fundamental question is whether the nanopores should mimic the hydration properties of specific ions and molecules to facilitate their transfer from solution to the nanopore interior. A nanopore that provides the same solvation free energy to an ion as liquid water is expected to promote fast ion permeation. It is less clear whether a nanopore that matches local hydration structure is needed to provide that matching solvation free energy. To address this question, we first applied ab initio molecular dynamics (MD) simulations to interrogate hydration structure of several metal ions in water. Our results on local hydration structure agree with scattering experiments and indicate that water hydrates each ion differently. That result supports the argument that local hydration structure is a differentiating feature of metal ions. But to explain how two ions with different hydration structures may act as analogues and permeate the same nanopore, a more restrictive definition of local hydration is needed. Next, we interrogated ion solvation in synthetic nanopores. A comparison of hydration vs solvation structure in synthetic and biological nanopores suggests that hydration mimicry is not necessarily the best strategy for fast transport.

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Nucleation and dissolution of NaCl crystals in aqueous solution

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Molecular dynamics simulations employing large systems (up to 100,000 particles) are used to investigate the mechanisms of crystal nucleation and dissolution in aqueous NaCl solutions. It is shown that crystal nucleation occurs via a two-step mechanism, similar to that which has been proposed for some other solutes such as proteins. The two sequential steps consist of a concentration fluctuation which results in a local region of high ion concentration, followed by spatial ordering. The first step occurs much more frequently than the second, such that spatial ordering determines the nucleation rate. We estimate that the critical NaCl nucleus contains 70-80 ions at ambient temperatures. The fact that the two-step mechanism applies to solutes as different as NaCl and proteins suggests that it is an important mechanism of homogeneous crystal nucleation. The dissolution of NaCl nanocrystals of varying size (up to 1400 ion pairs) and shape (cubes, spheres, rods, and tablets) is also investigated. The dissolution rate and mechanism is shown to strongly depend on these physical variables. Interestingly, however, in some cases conventional macroscopic rate laws are shown to apply until the crystal size is reduced to a few hundred ion pairs.
To explain why dynamical properties of an aqueous electrolyte near a charged surface seem to be governed by a surface charge less than the actual one, the canonical Stern model supposes an interfacial layer of ions and immobile fluid. However, large ion mobilities within the Stern layer are needed to reconcile the Stern model with surface conduction measurements. Modeling the aqueous electrolyte/amorphous silica interface at typical charge densities, a prototypical double layer system, the flow velocity does not vanish until right at the surface. The Stern model is a good effective model away from the surface, but cannot be taken literally near the surface. Indeed, simulations show no ion mobility where water is immobile, nor is such mobility necessary since the surface conductivity in the simulations is comparable to experimental values. Biomolecules near silica and the dynamics of the electrical double layer near biomolecules will all be discussed.

**COLL 326**

**Coaxial lithography**

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Optical and electrical properties of heterogeneous nanowires are profoundly related to their composition and geometry at the nanoscale. Until now, the intrinsic limitations of conventional lithographic techniques have drastically limited the range of multi-compositional nanowires that can be made. Post-modification of pre-synthesized nanowires has been the only way to generate coaxial structures, offering no control over
both the length and location of the shell along the nanowire. For example, the ability to
tune the shell composition along the wire axis to generate asymmetric nanowires, still
remains a synthetic challenge. Herein, we report a high-throughput technique, termed
coaxial lithography, bridging templated electrochemical synthesis and lithography for
fabricating coaxial nanowires in a parallel fashion with sub-10 nanometer resolution in
both linear and radial dimensions. Various combinations of coaxial nanowires
composed of metals, metal oxides, metal chalcogenides and conjugated polymers were
fabricated using this procedure. The optoelectronic properties of a plasmonic nanoring
embedded hybrid core-shell semiconductor nanowire were studied. Integration of
plasmonic nanorings within p-n type core-shell semiconductor nanowires demonstrates
the potential of this new synthetic technique to radically change the nanowire
fabrication, in terms of the types of structure that can be envisioned, synthesized, and
tested in the laboratory.

COLL 327

Spectroelectrochemistry of plasmonic nanoparticles

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Despite attempts to understand the effect of nanoparticle surface charge density on
catalytic activity, controversy still remains, likely because of the sample heterogeneity
that is intrinsic to ensemble measurements. To overcome this problem, a direct
correlation between electrochemical activity and nanoparticle morphology and surface
chemistry on the single particle level is required. In this work, the intrinsic surface
plasmon resonance of gold nanoparticles is exploited as a high sensitivity local reporter
on local charge density. To achieve single particle spectro-electrochemical microscopy,
we performed single particle dark-field scattering spectroscopy of 20 - 50 nm gold
nanoparticles in an electrochemical cell and monitored the charging and discharging of
single nanoparticles through changes in the surface plasmon resonance that sensitively
depends on the nanoparticle electron density.

COLL 328

How events at the nano/bio interface determine advantageous or adverse
biological outcomes

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This talk will discuss how events at the nano/bio interface determine advantageous or
adverse biological outcomes.

COLL 329
Towards the prediction of solution-phase gold nanoparticle stability

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Implications of surface chemistry variations on metal nanoparticles (i.e., packing density, tilt angle, and composition) influence not only the optical and electrical properties of these materials but also their behavior in complex environments. Herein, the combination of theoretical predictions with straightforward experimental measurements supports and describes the observed electrical and optical properties of gold nanomaterials using interaction pair potential modeling. Specifically, a semi-empirical solution to extended DLVO theory is derived using synergistic contributions from a size-dependent Hamaker constant for gold, interfacial surface potentials, and tilt angles of self-assembled monolayers account for van der Waals, electrostatic, and steric interactions between carboxylic acid functionalized gold nanoparticles in solution. Such molecular level insight into surface chemistry directed nanostructure-property relationships are envisioned to improve the systematic use of solution-phase nanomaterials by providing a method for predicting the thermodynamic stability of nanomaterials in various environmental conditions.

COLL 330

Surface chemistry and photoluminescence of small metal nanoparticles

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Theory and experiment indicate that discrete noble metal nanoparticles with diameters between 2 and 3 nanometers (nm) are metallic, yet these particles are known to display bright photoluminescent properties that can be tuned by changing particle composition. Here, we report the impact of surface chemistry on these optoelectronic features for a variety of different metal compositions. Specifically, we investigate the role of small molecule ligands on photoluminescent figures of merit including excitation and emission maxima, quantum yield, and lifetime. Using a combination of surface analysis and molecular characterization techniques, we show that the identity, quantity, and solvent compatibility of these organic ligands can influence each aspect of particle PL properties. The impact of this surface chemistry on their utility in bioimaging and reaction-tracking applications will also be discussed.

COLL 331

Influence of the protein corona on gold and diamond nanoparticle interaction with model cell membranes
The large increase in the production and use of engineered nanoparticles has resulted in increased potential for organismal exposure to these nanoparticles. The growing probability of exposure has led to an increasing interest in the interaction between engineered nanoparticles and biological macromolecules. Nanoparticles introduced into biological systems (e.g., digestive tract, blood stream, cytoplasm) acquire an ensemble of adsorbed biomolecules referred to as the “biomolecular corona.” As a first step in exploring the effect of biomolecular coronas on nanoparticle interactions with cell membranes, we have investigated the acquisition of protein coronas by gold and diamond nanoparticles bearing differing functionalizations and their interaction with model cell membranes using quartz crystal microbalance with dissipation monitoring. We find that acquisition of a protein corona significantly changes nanoparticle interaction with model cell membranes.

**COLL 332**

**Minimizing nonspecific nanoparticle interactions via zwitteration**

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Minimizing nonspecific interactions of nanoparticles with natural and engineered interfaces is an essential prerequisite to the design of specific interactions or targeting applications. If their surfaces cannot be masked efficiently, nanoparticles tend to agglomerate, adhere, or precipitate prematurely. Typical strategies for maintaining nanoparticle stability in vitro or in vivo employ neutral polymers or oligomers physically or chemically bound to the surface. For example, oligomeric or polymeric ethylene glycol (PEG) endows stability and enhances circulation times. We have developed a monomeric sulfobetaine zwitterion motif for decorating nanoparticle surfaces. These small, water-soluble reagents have been chemically attached to the surfaces of gold, silica and iron oxide nanoparticles using thiol or siloxane chemistry. The protected nanoparticles are highly stable when challenged with salt or proteins. We will describe the synthesis and properties of these nanomaterials, and we will explore the fundamental science behind the excellent nonfouling properties of the zwitterion surface.
Regressing metastatic and drug resistant breast cancer with triggerable pronifuroxazide nanoparticle by inhibiting transcription factor STAT3

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Cancer chemotherapy is judged effective when it reduces tumor burden by blocking the proliferation and inducing apoptosis of cancer cells. In practice, often it recurs or metastasizes shortly after the primary tumor has been exterminated. Cancer stem cells are reported to be controlled by pathways that are dormant in normal adult cells, e.g. PTEN, which is a negative regulator of transcription factor STAT3. STAT3 regulates genes that are involved in stem cell self-renewal and thus represents a novel therapeutic target of significant clinical importance.

This work, for the first time, reports a nanomedicine strategy for selective and safer delivery of STAT3 inhibitors designed towards metastatic and drug resistant breast cancer. We have synthesized a novel lipase-labile SN-2 phospholipids-pro-drug from a clinically investigated inhibitor, nifuroxazide, which is regioselectively cleaved by the membrane abundant enzymes in cancer cells. Pro-nifuroxazide was used to formulate the nanoparticles (Pro-nifuroxazide NP) and the cytotoxic ability of pro-nifuroxazide NP (80±5nm) was screened in ER(+-)MCF-7 and ER(-)-MD-MB231 cells at 48h-72h using MTT proliferation assay. Results indicated that pro-nifuroxazide NP are at least fivefold more effective towards inhibiting ER(+-)-MCF-7-cells in a time dependent manner compared to parent nifuroxazide. This presentation will discuss the synthesis of the prodrug, its self-assembly into a nanoparticle, physico-chemical characterization of the, their cellular toxicity assays and further biological studies to confirm abolition of stem cell-subpopulation.

Novel chemoradiotherapeutic magnetic nanoparticles for targeted treatment of non-small cell lung cancer

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Lung cancer is the leading cause of cancer-related death in the United States and 85% of all lung cancers are classified as non-small cell (NSCLC). Unfortunately, NSCLC is extremely difficult to treat and the survival rates are low; in 2012, the five year survival rate was only 17%. An innovative approach that may ultimately allow for the clinician to target and aggressively reduce tumor burden in patients with NSCLC will be presented. Platinum (Pt)-based radiosensitizers; cisplatin, carboplatin, oxaliplatin and holmium-166 radionuclide (166Ho; $E_{\text{β-max}}=1.84$ MeV; $t_{1/2}=26.8$ h) have been incorporated in a garnet magnetic nanoparticle (Pt-HoIG) for selective delivery to tumors using an external magnet. The Pt anticancer drugs can be used as radiosensitizers, and the $^{166}$Ho emits beta particles and gamma photons, which can be used for therapy and imaging, respectively. A major obstacle in therapy is the non-specificity of current treatments. Nonspecific anticancer drugs administered via intravenous injection are distributed throughout the entire body and are harmful to healthy tissues as well as tumor sites, leading to significant side effects. The nanoparticles reported here could potentially deliver their chemoradiotherapeutic ‘cargo’ directly to tumors in a patient, guided by a magnet. The HoIG and Pt-HoIG nanoparticles were characterized using PXRD, SEM, EDX, TEM, ICP-MS, and Zeta potential measurements. Neutron activated cisplatin-HoIG and oxaliplatin-HoIG showed greater toxicity than HoIG, free cisplatin and oxaliplatin toward NSCLC A549 cells. Thus, cisplatin and oxaliplatin act synergistically with the radioactive Ho making nontoxic doses of radiation extremely effective.

COLL 335

Controlled and safer therapeutic delivery of venom toxins using well-defined polymeric nanoparticles for cancer inhibition

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Myriad of advancement has been made to identify naturally abundant substances for use as therapeutic agents. Host defence peptides (eukaryotic cells) from animal venoms have been identified to possess substantial anticancer properties. However, their therapeutic potential cannot be fully realized without a controlled delivery mechanism because of off-target toxicity, non-specificity, complement activation issues and unfavorable pharmacokinetics, all contributed to negatively to translate these agents to clinic. Towards a safer, translatable approach, we have developed a viable chemical methodology based on well-defined, self-assembled polymeric nano-architecture for controlled delivery of venom peptides.

Although our methodology is applicable for peptides of 5-30 aa, as a specific example, a well-studied cytolytic peptide, Melittin (26 aa), was selected for preliminary studies. The melitin-incorporated polymeric nanoparticles (hydrodynamic diameter: $50 \pm 5$nm) were
prepared by applying a post-incubation methodology. The parent nanoparticles were self-assembled as aqueous suspension of amphiphilic diblock-co-polymer PS-b-PAA and Polyoxyethylene (20) cetyl ether. These particles showed significant stability over time and the release of melittin remained well controlled in time and concentration dependent manner. The cytotoxicity of these nanoparticles was studied in MCF-7 and MDA-MB231 breast cancer cells using MTT assay and showed IC_{50} value of 50nM. This construct promises to address the serious off-target toxicity of the membrane-bound venom peptides when systemically delivered and simultaneously protects the integrity of the peptide itself that may complicate systemic application. The presentation will discuss characterization and application of these particles using dynamic light scattering, atomic force microscopy, transmission electron microscopy, electrophoretic potential, and cytotoxicity analysis. We anticipate this unique anticancer agent found in nature coupled with the delivery approach has the potential for the development of a novel anticancer treatment.

**COLL 336**

**Discovery of novel polymeric platinum nanoparticles for targeted drug delivery**

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In this work, we seek to develop a new method for the delivery of therapeutics *in vivo*. Our project investigates the inclusion of covalently bound, known anticancer platinum complexes into tumor-targeted nanoparticles.

The novel element is the covalent linkage of the metal complexes to the polymer, since they are monomers themselves and can therefore be directly polymerized providing a means for greater control of how much platinum is included in the particles. This feature ensures both optimized and controlled platinum loading of the nanoparticles in an unprecedented fashion. Such excellent control and ease of characterization should not be underestimated when considering a program seeking to optimize a nanoparticle system for *in vivo* use.

The synthesis, characterization, *in vitro* drug release and cytotoxicity are part of our first set of studies to put this type of nanoparticles as a new platform for delivery systems of platinum-based drugs.

**COLL 337**

**Development of phosphonium-based shell-crosslinked knedel-like nanoparticles for gene delivery**
Safe and efficient vectors for gene delivery are eagerly sought to enable the realization of the full potential of gene therapies. Several recent reports in the literature have shown that phosphonium-based polymers could represent an efficient and less toxic alternative to the ubiquitous polyammoniums for siRNA and DNA delivery applications. We have developed a new diblock copolymer based on the degradable polyphosphoester-block-poly-(L-lactide) (PPE-b-PLLA) skeleton, functionalized with trialkylphosphonium side groups via a thiol-yne click reaction. The synthesis of clickable 2-mercaptoethyltrialkylphosphonium salts is described, and it is shown that bulky phosphonium salts bearing long alkyl chains (butyl and ethyl) performed poorly in thiol-yne reactions, whereas the trimethylphosphonium derivative added more efficiently.

Preliminary investigations on the diblock have confirmed its low toxicity towards 293T cells. An Alexa Fluor® 488 dye (A488)/polymer conjugate has been synthesized by Cu-assisted azide-alkyne click chemistry to allow for the tracking of the polymer in cell transfection experiments. The supramolecular assembly of the copolymer strands into spherical micellar aggregates has been confirmed by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Thiol-ene/yne click reactions were performed to crosslink the shells of non-dye-labeled micelles using a PEG-based dithiol to yield
novel phosphonium-based cSCKs that were evaluated for their toxicity, binding efficiency towards DNA and siRNA, and transfection efficiency.

Molecular thera beacon for next generation UV therapy

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Psoralens and ultraviolet light A (PUVA) is one of the traditional phototherapies for psoriasis: An autoimmune disease that triggers raised, red, itchy patches on the skin. Psoralens are either taken orally or applied topically to the affected area before the administration of a phototherapy. However, the prolong usage of PUVA has been showed to be photochemically genotoxic and increase the risk of melanoma. An improved, safer yet efficacious PUVA therapy is the unmet need.

To this end, we propose a molecular thera becon comprising of psoralen as a reactive oxygen species generator and a-tocopherol as a quencher. The beacons were designed to have an optically active carbon nanoparticle platform with a hydrodynamic diameter approx. 10 ± 1 nm that can solely be activated at the targeted melanoma cells without having significant adverse effects on normal tissue. Carbon nanoparticles were derived from a natural source (i.e. cane sugar) and surface passivated with a polyethyelenglycol-conjugated a-tocopherol. With the masking effect of alpha-tocopherol, the phototoxicity of psoralens is suppressed until their intracellular deliver and pH dependent release of the quencher in cancer cells. The release of psoralens to the targeted area is controlled by the ester linkage between the ROS quencher and the surface passivating PEG1000. Once reaching the target, the ROS quencher frees from nanoparticles due to the more acidic environment of cancer cells, which induces the breakage of the ester bond, activating the psoralen molecules. The synthesis, physicochemical characteristics of the beacons including dynamic light scattering, atomic force microscopy, transmission electron microscopy, electrophoretic potential will be discussed in this talk. Moreover, the relative cytotoxicity of these improved 'on-off' PUVA-agents with traditional psoralens on melanoma cells under the presence or absence of UVA treatment will be discussed to elucidate the effect of our design.
A novel biodegradable star-shaped poly-asparamide was developed for gene delivery. We discovered that the star-shaped polymer showed higher gene transfection efficiency in cell culture than the linear counterparts. What is more intriguing is that the plasmid DNA nanoparticles formed with the star polymer can specifically deliver the gene to the lung in mice and completely avoid the liver accumulation, where most of the nanoparticle delivery systems end up with. In contrast, the plasmid DNA nanoparticles formed with the linear polymer can only accumulate in the liver and express the gene with much lower efficiency. This novel star polymer is applied in an orthotopic lung cancer model to knockdown oncogenes in order to overcome drug resistance.

**COLL 340**

**Ionic conjugated polymer nanoparticles and their application in visualizing cancer cells**

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We reported the development of novel ionic conjugated polymer-lipid nanoparticles (PLNP) by harnessing the interaction of ionic conjugated polymer and counter ionic lipid as well as the self-assembly of the formed polymer-lipid complex. Compared to the bulk conjugated polymer material, these nanoparticles possess enhanced fluorescence efficiencies in solution, show strong fluorescence in solid phase, and resistance to photo-bleaching upon photo-illumination. In addition, the fluorescence spectrum of the nanoparticles are blue shifted when the size of the particles decreases, a size dependent fluorescence property in conjugated polymer based nanoparticles that was observed for the first time. Considering the advantage of transfection function of the lipid, we studied the interaction of PLNP with cells. It was found that PLNP could accumulate within the cancer cells (Skov3) very efficiently to yield brightly fluorescent cells while very limited cellular uptake was observed in normal cells (End1). Preliminary mechanism study indicated that the contrasting cellular uptake of PLNP in cancer cells might be due to enriched lipid-cholesterol raft, which plays critical roles in endocytosis, in cancer cells. The results demonstrate the potentials of PLNP as a unique fluorescence material for bio-system visualization and for differentiating cancer cells from normal cells.

**COLL 341**

**Theranostic anticancer agents based on internally functionalized ORMOSIL nanoparticles**
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We prepared organically modified silica (ORMOSIL) colloidal particles with internal functional groups and microporosity, suitable for the incorporation of modalities for both MRI imaging and cancer treatment by neutron capture therapy using boron-10 and gadolinium-157 nuclei. These modalities were incorporated by preparing ORMOSIL particles with reactive functional groups throughout the nanoparticle body, followed by their conversion into the metal chelating and boron-containing moieties inside the nanoparticles. For gadolinium-157 chelation, diethylenetriamine groups were introduced and converted to diethylenetriametetraacetic acid groups by facile alkylation with bromoacetic acid under basic conditions. To incorporate boron-10, internal vinyl groups were introduced and underwent hydroboration under mild conditions with high degrees of conversion. Furthermore, pH-sensitive carbamate linkages were incorporated into the particles to render them biodegradable, and nanoparticle porosity was controlled by templating the particles with tannic acid. This talk will describe in detail the preparation, characterization and properties of the resulting theranostic colloidal particles.

COLL 342

Fliposomes: Stimuli-triggered conformational flip of novel amphiphiles causes an instant cargo release from liposomes

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New developments are presented in the design of stimuli-responsive liposomes for targeted delivery via the construction of a liposome membrane (lipid bilayer) using amphiphiles able to perform a stimuli-triggered conformational flip (“flipids”). When done simultaneously by a major or significant part of the bilayer molecules, this massive flip disrupts the liposome membrane and induces a rapid release of the liposome load specifically in response to the initial stimulus. The conformational switches incorporated into the amphiphilic molecules could potentially be controlled by various internal or external factors (pH, metal complexation, light, etc.). Using this concept we designed a series of pH-triggerable “flipids”, and prepared and tested “fliposomes” with extraordinary characteristics: high stability in storage and in serum combined with an instant release of their cargo in response to a weakly acidic medium.

COLL 343

Role(s) of adsorbed water in the surface chemistry of environmental interfaces in the atmosphere
The chemistry of environmental interfaces such as oxide and carbonate surfaces under ambient conditions of temperature and relative humidity is of great interest from many perspectives including heterogeneous atmospheric chemistry. Adsorbed water plays an important role in the reaction chemistry of oxide and carbonate surfaces with trace atmospheric gases. The focus of this talk is on the multi-faceted roles of adsorbed water can play in the chemistry of environmental interfaces in the atmosphere. These reactions are complex and the role of adsorbed water is found to depend on the details of the reaction mechanism and the coverage of water on the surface as will be discussed through several examples including the surface chemistry of organic acids.

**COLL 344**

**Enhancement in optical properties of dust upon mixing with dicarboxylic acids**

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Aerosols in the atmosphere are chemically complex based on their formation and processing. In the laboratory, building this complexity into atmospheric proxies while still maintaining control over variables is useful for improving understanding of aerosols in various environments. Using cavity ring down spectroscopy at 532 nm, we measured the extinction enhancements in size selected montmorillonite upon mixing with three atmospherically relevant dicarboxylic acids - glutaric, succinic and malonic acids. Extinction was measured at four accumulation mode sizes under dry and elevated relative humidity (RH) for each case. The results reveal evaporation from pure glutaric acid particles. Malonic acid-montmorillonite mixtures show dramatic increases in extinction at high RH, while other mixed systems studied show less change. Mie theory calculations have been completed to compare homogeneous or core-shell internal mixture and external mixtures with experimental results. These results improve our understanding of how dust aerosols interact with light as chemical complexity increases.

**COLL 345**

**Analysis of solid and liquid surfaces using FT-IR spectroscopy**

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Infrared reflection-absorption spectroscopy (IRRAS) provides information about the surface chemistry and how it changes under the influence of gas phase. Since gas above the surface of interest is also absorbs in the mid-infrared, it can interfere with the
measurement of very small peaks due to surface chemistry. To achieve the best results, the FT-IR spectrometer must be capable of keeping the gas vapor interference to a minimum. Polarization-modulation IRRAS (PM-IRRAS) technique is used to remove gas absorption interference from surface spectra. Typical IR absorbances of a monolayer in an PM-IRRAS experiment are about $10^{-3}$ – $10^{-4}$ a.u. Detection of such small absorbances calls for an FT-IR spectrometer that can provide high signal-to-noise ratios in a short acquisition time. The other important requirements for an FT-IR for surface science include high dynamic range and low baseline drift. Recent advances in FT-IR PM-IRRAS spectroscopy will be reviewed in this presentation and optimization of experimental setup will be discussed. Examples of application will include kinetics of chemical changes on metal surfaces exposed to regular lab air and proteins structure at the air-water interface.

**COLL 346**

**Complexation and photodegradation of catechol to iron(III) as a model for multicomponent aerosol systems**

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Surface water plays a crucial role in facilitating or inhibiting surface reactions in atmospheric aerosols. Little is known about the role of surface water in the complexation of organic molecules to transition metals in multicomponent aerosol systems. We will show results from real time diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments on the in situ complexation of catechol to Fe(III) and its photosensitized degradation under dry and humid conditions. Catechol was chosen as a simple model for humic-like substances (HULIS) in aerosols and aged polyaromatic hydrocarbons (PAH). It has also been detected in secondary organic aerosols (SOA) formed from the reaction of hydroxyl radicals with benzene. Given the importance of the iron content in aerosols and its biogeochemistry, our studies were conducted using FeCl3 as a source for soluble Fe(III). For comparison, these surface-sensitive studies were complemented with bulk aqueous ATR-FTIR, UV-vis, HPLC, and LC-ESI-MS measurements for structural, quantitative and qualitative information about complexes in the bulk, and potential degradation products. The implications of our studies on understanding interfacial and condensed phase chemistry relevant to multicomponent aerosols, water thin islands on buildings, and ocean surfaces containing transition metals will be discussed.

**COLL 347**

**Environmental molecular chemistry of atmospheric particles**

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Fundamental understanding of the complex chemistry of atmospheric aerosols, their physico-chemical properties and environmental impacts is a challenging task because no single method of analytical chemistry is capable of providing the full range of analytical chemistry information. Electron microscopy and micro-spectroscopy approaches can visualize individual particles and their internal structures; however, they largely exclude molecular-level information, and are limited to elemental and chemical bonding characterization. Contemporary methods of high-resolution mass spectrometry can provide detailed information on the molecular content of organic aerosol, but these methods use bulk particle samples and provide no knowledge of the individual particle composition. Therefore, application of complementary analytical methods of chemical analysis is necessary for comprehensive characterization of aerosol properties ranging from bulk molecular composition of aerosol organic constituents to microscopy level details of individual particles. Combined assessment of the results provided by complementary analytical chemistry techniques offers unique insights to understand the composition and physico-chemical properties of organic aerosols determining their effects on air quality and climate. This presentation will give an overview of recent field and laboratory studies of atmospheric aerosols conducted by the presenter and his colleagues with an overall goal to understand fundamental relationship between chemical transformations of atmospheric organic particles and their environmental and climate impacts.

COLL 348

Computational studies of the role of water in the formation and reaction of NOx species

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The recent report of a new NOx source through photoinitiated oxidation of ammonia at TiO₂ surfaces prompted study of the proposed reaction intermediates and the interaction with water.¹ Reaction of the NH₂ radical, which can be generated from ammonia at an irradiated TiO₂ surface, with O₂ to form NO and H₂O is insignificant in the gas phase. However, experimental studies suggested this process could contribute to tropospheric NOx concentrations when catalyzed by water. Quantum chemical calculations on relevant species in water clusters, which may provide a model of the water surface, confirmed the stabilization of key reaction intermediates. The hydrogen bonding structure of the cluster provides a means for isomerization through proton transfer along water wires lowering reaction barriers. Computational studies also continue to provide molecular level description of proposed steps in the long-studied surface hydrolysis of NO₂.

COLL 349

Working hypothesis on the mechanism of the synergic adverse effects of ambient ozone and PM$_{2.5}$ particulates

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The pulmonary epithelium is protected against atmospheric ozone O$_3$(g) by a fluid film (ELF) containing ascorbic acid (AH$_2$) and related antioxidants. This mechanism of protection however fails if co-pollutants redirect AH$_2$ and O$_3$(g) into species that can transduce oxidative damage to underlying tissues. We have shown (Enami et al., PNAS 2008) that, whereas the ozonation of ascorbate AH$_2$ [pK$_a$(AH$_2$) = 4.1] under physiological conditions yields innocuous dehydroascorbic acid, the ozonation of AH$_2$ in pH < 5 acidic media generates a cytotoxic ozonide. On this basis we speculated that acidic particulates, by acidifying ELF below its normal pH = 6.9 value, would disable its protective antioxidant function. Here we refine our proposal by showing that the typical buffer capacities of ELF’s (~ 10 mM/pH) prevent their direct (chemical) acidification by the inhalation of polluted ambient air containing representative acidic particulate loadings (< 100 mg/m$^3$). We propose instead, on the basis of extensive clinical and physiological studies on the innate lung host defense response, that ELF acidification is mediated by inflammatory reaction to acidic particulates. On this basis, ultrafine particulates, which reach the alveoli whose ELF is ~ 50 times thinner than that of the airways, are expected to be pose a particularly aggressive challenge to underlying alveolar macrophages.

COLL 350

Surfaces of aerosol particle material from southern Finland, Amazonia, and California studied by vibrational sum frequency generation

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We summarize and compare the analysis of the surfaces of natural aerosol particles from three different forest environments by vibrational sum frequency generation. The experiments were carried out directly on filter and impactor substrates, without the need for sample preconcentration, manipulation, or destruction. We discuss the important first steps leading to secondary organic aerosol (SOA) particle nucleation and growth from terpene oxidation by showing that, as viewed by coherent vibrational spectroscopy, the chemical composition of the surface region of aerosol particles having sizes of 1 μm and lower appears to be close to size-invariant. We also describe how the combination of
aerosol science, advanced vibrational spectroscopy, meteorology, and chemistry can be highly informative when studying particles collected during atmospheric chemistry field campaigns, such as those carried out during HUMPPA-COPEC-2010, AMAZE-08, or BEARPEX-2009, and when they are compared to results from synthetic model systems such as particles from the Harvard Environmental Chamber (HEC). Discussions regarding the future of SOA chemical analysis approaches are given in the context of providing a path toward detailed spectroscopic assignments of SOA particle precursors and constituents on SOA particle surfaces.

COLL 351

Molecularly engineering cell-surface interfaces

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Supramolecular chemistry provide nowadays an excellent prospect to construct reversible biological interfaces that can be employed for supramolecular cell manipulation experiments. Making use of supramolecular chemistry is rewarding to develop functional materials and devices. Knowing the limitations involved in ordering proteins at different length scales will surely hasten developing future applications, supramolecular bionanotechnology being the most prominent. The construction of synthetic supramolecular assemblies of proteins provides an excellent tool to fabricate organized bioactive components at surfaces. I will present new synthetic procedures for site-specific noncovalent anchoring of proteins to surfaces and polymers. Special attention is paid to orientational and conformational aspects at the surface and will be demonstrated. Using concepts of multivalency the interactions between proteins and surfaces can be modulated by design. Many of the protein complexes were patterned on surfaces using microcontact printing or nanolithography and visualized using fluorescence microscopy. Furthermore, supramolecular linkers that are sensitive to remote electrochemical stimuli will be presented, using cucurbituril (CB) and cyclodextrin (CD)-modified surfaces. Electrochemical switching was studied using surface embedded electrodes. Cell release was studied in detail in the case of cell-adhesive peptides and growth factors. Lastly, supramolecular linkers were compared to reversible covalent linkers providing insight in the cell receptor signaling pathway. With the development of reversible bioactive platforms on surfaces serving as a reversible dynamic interfaces to cells, improved scaffolds for tissue regeneration will become in hand. First steps into this directions will be introduced as well.

COLL 352

Supramolecular engineering of bioelectronic nanostructures derived from the assembly of pi-conjugated oligopeptides

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Biologically compatible electronic materials will play major roles to bring semiconductor properties to bear on current problems in biosensing and tissue repair. Unfortunately, the use of organic electronic materials has been very limited relative to traditional inorganics due to perceptions of material degradation or solubility problems. We developed synthetic approaches to incorporate a wide variety of pi-conjugated functionality into the backbones of water-soluble peptides, such as fluorophores, reactive polymer precursors, and typical n-type and p-type semiconductors. These molecules self-assemble in aqueous media into 1-D nanomaterials with diameters under 10 nm and lengths of microns. These materials ultimately lead to the formation of self-supporting hydrogels that can be prepared with either randomly dispersed or globally aligned nanostructure components. In this presentation we will describe the synthesis and optoelectronic characterization of these new nanomaterials using electronic spectroscopy and their integration into functional bioelectronic transistors. Prospects for using the peptide sequences to elicit biological adhesion or other specific responses will be addressed.

COLL 353

Supramolecular nanoparticles (SNPs) for molecular diagnostics and therapeutics

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In this talk, the convenient, flexible and modular synthetic approach for supramolecular nanoparticles (SNPs) and their application in the biological field will be introduced. The main challenge for researchers is in designing a platform that is compatible with the complexity of living systems. As compared to the conventional synthetic method of nanoparticles that is often time consuming, tedious, and limiting in its ease of generating a diverse set of sizes and unique surface chemistry, supramolecular chemistry combines the twin concepts of self-assembly and molecular recognition to easily generate unique nanostructured materials from the non-covalent bonding of the same small set of molecular building blocks. In our system, the cyclodextrin/adamantane (CD/Ad) recognition was employed to achieve self-assembly of SNPs from three different molecular building blocks: (i) Ad-grafted polyamidoamine dendrimer, 8-Ad-PAMAM, (ii) β-Cyclodextrin-grafted branched polyethylenimine, CD-PEI, and (iii) Ad-functionalized PEG compound, Ad-PEG. The three-component supramolecular approach offers synthetic convenience, flexibility, and modularity to alter the sizes and the surface chemistry of the SNPs. The uniqueness of this self-assembly approach is that it allows the surfaces of the SNPs to be decorated with various targeting ligands, while offering flexibility in the selection of many different loadings. These tailored SNPs achieve desired mechanical and functional properties and are widely applied for the diagnosis and therapy of diseases.
Supramolecular self-assembly for fluorescence imaging inside living cells

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Hydrogels are widely used in many applications such as tissue engineering, regenerative medicine, and drug delivery. To produce new bimimetic materials (e.g., scaffolds) with tailored structure and properties requires a better understanding of the self-assembly behavior of small gelator molecules in the biological environment. There are two major approaches to study the self-assembly process. In the first, the hydrogelator is covalently labeled with a suitable fluorophore, and the self-assembly process aligns both the hydrogelator molecules and the appended fluorophores into nanofibers. The second approach does not require labeling of the molecules of interest. It is based on correlative light and electron microscopy (CLEM) investigation of the self-assembly of small molecules in their native form inside mammalian cells. Both methods allow us to determine the formation, localization, and progression of molecular assemblies generated from small molecular hydrogelators by an enzyme-triggered hydrogelation mechanism in cells. Previously, we demonstrated how the precursors go into the cell, where the molecular assembly occurs, and we determined the interaction between molecular assemblies and cellular organelles. This work establishes a general strategy to describe the spatiotemporal profile of molecular assemblies inside cells. A new model system is used to mimic cellular mechanisms and processes related to endogenous-normal and aberrant-protein nanofibers.

Formation of protein cage clusters by cationic linkers

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The organization of nanoparticles into ordered structures is affected by a multitude of forces which complexes the construction of programmable nanomaterials in this way. Supramolecular protein cages can be used both as model systems and as functional building blocks for the formation of such clusters of nanoparticles. In this contribution the clustering of Cowpea Chlorotic Mottle Virus (CCMV) based protein cages using gold nanoparticles is discussed. The binary particle systems formed by this means rely in their formation on the protein cage symmetry. The protein cage symmetry in turn, can be influenced by the material encages in it, which eventually may lead to the controlled formation of functional supramolecular materials.
Coll 356

Supramolecular particles in nanomedicine

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Supramolecular nanostructures are attractive for nanomedicine since co-assembly of molecules can be used to integrate the necessary mechano-chemical characteristics with targeting and therapeutic functions. Molecular design can also be used to program their biodegradation into useful structures such as nutrients without having to rely on clearance or the risk that harmful nanoparticles may hide inside cells. From a therapeutic standpoint, supramolecular nanoparticles based on peptides offer the possibility of increasing their half-life, which could be problematic in the clinical implementation of potential biologics. Given all these attributes they could revolutionize disease treatments with greater efficacy and the elimination of serious side effects. This lecture describes the development of novel peptide amphiphile filamentous nanostructures that can be targeted to injured arteries and chemically designed to deliver nitric oxide in order to avoid neointimal hyperplasia after stent placement. The lecture will also describe supramolecular nanostructures that can be targeted to specific receptors expressed in cancer cells while also carrying chemotherapy cargo in their hydrophobic compartments. Other examples will describe supramolecular particles to deliver nucleic acids and deliver cells for a broad range of therapies in regenerative medicine.

Coll 357

Self-assembly of hybrid nanoparticles directed by light and magnetic field

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Self-assembly is emerging as a superior method to prepare adaptive and responsive nanomaterials. In this contribution we report a soft hybrid material composed of superparamagnetic nanoparticles and cyclodextrin vesicles which self-assemble in microscale linear aggregates in aqueous solution under the influence of a magnetic field. The metastable linear aggregates can be stabilized by a noncovalent and photoresponsive cross-linker, which can be photoisomerized between an adhesive and a nonadhesive configuration. Thus, the hybrid material responds to magnetic field as well as to light and a stable self-assembled structure can only be obtained in a magnetic field in the presence of the noncovalent cross-linker. We have recently extended this strategy to the dynamic assembly of superparamagnetic nanoparticles modified with cyclodextrin. These hybrid nanoparticles can be further functionalized using host guest interaction and molecular recognition.
Photochemistry of CO, acetone and O₂ on reduced rutile TiO₂(110)

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We have investigated the ultraviolet (UV) photon-stimulated reactions of CO, acetone and oxygen adsorbed on TiO₂(110). The O₂ photochemistry depends on the coverage. For small coverages, only ~14% desorbs while the rest either dissociates during UV irradiation, or remains molecularly adsorbed on the surface. For the maximum coverage of chemisorbed oxygen, the fraction of O₂ that photodesorbs is ~45%. While photo-generated holes are responsible for the O₂ photodesorption, photo-generated electrons are responsible for the photo-induced O₂ dissociation. When CO is co-adsorbed with O₂, CO₂ is produced during UV irradiation. The CO₂ preferentially desorbs in the plane perpendicular to the bridge-bonded oxygen (BBO) rows at an angle of 45°. Furthermore, the production rate of CO₂ is zero when the UV irradiation starts and reaches a maximum value at intermediate times before decaying at longer times. The results demonstrate that the photooxidation of CO is a multi-step reaction that proceeds through a metastable intermediate state that is oriented perpendicular to the BBO rows. This state is consistent with an O-O-C-O state found via density functional theory. For acetone co-adsorbed with oxygen, previous research suggests that a thermal reaction between acetone and adsorbed oxygen to form an acetone diolate precedes the photochemistry. During UV irradiation, a methyl radical is ejected leaving acetate on the surface. Using infrared reflection absorption spectroscopy (IRAS), we have identified the acetone diolate. We have also measured the angular distribution of the photodesorbing methyl radicals. Consistent with its ejection from acetone diolate, we observe a peak in the distribution at ~45° in the plane perpendicular to the BBO rows. However, a second photodesorption peak normal to the surface indicates that a second reaction channel is available. In general, these studies provide new insights into mechanisms responsible for the photochemistry of small molecules on TiO₂.

Combined theoretical and experimental studies of structures and activities of rutile TiO₂ surfaces

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TiO$_2$ is one of the most important metal oxide materials and finds applications in a wide range of fields such as catalysis, photocatalysis and biomaterials. It is also often used as model catalysts in surface science studies aiming at elucidating some fundamental aspects in catalytic processes of metal oxides. Among its different polymorphs, rutile TiO$_2$ 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 TiO$_2$, namely TiO$_2$(110) and (011), by performing combined theoretical DFT calculations and experimental STM measurements. We have found that for rutile TiO$_2$(110), the adsorption and kinetic performance of various molecules is largely determined by surface conditions, especially the hydrogenation caused by their own dissociation. Moreover, the surface sites along separated rows provide well-ordered accommodation patterns for adsorbates, and the inter-molecular interactions may further promote the formation of regular adsorption structures. For the rutile TiO$_2$(011) with unique reconstructed conformation, its structures can undergo further restructuring upon interaction with various molecules, which can dramatically affect its activity. In addition, due to its specific orientation, the (011) facet has fluent link with structural channels in the bulk, exhibiting unique properties in surface-bulk-related dynamic processes.

**COLL 360**

**TiO$_2$/ferroelectric heterostructures as dynamic polarization-promoted catalysts for water oxidation**

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Using first-principles density functional theory (DFT) calculations, we explore the chemical activity of epitaxial heterostructures of TiO$_2$ anatase on strained polar SrTiO$_3$ films focusing on the oxygen evolution reaction (OER), the bottleneck of water-splitting. Our results show that the reactivity of the TiO$_2$ surface is tuned by electric dipoles dynamically induced by the adsorbed species during the intermediate steps of the reaction while the initial and final steps remain unaffected. Compared to the OER on unsupported TiO$_2$, the combined effects of the dynamically induced dipoles and epitaxial strain strongly reduce rate-limiting thermodynamic barriers and significantly improve the efficiency of the reaction.

**COLL 361**

**Oxidation reactions on the PdO(101) surface**

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Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this
talk, I will discuss our investigations of the surface chemical properties of a PdO(101)
thin film, focusing on the activation of alkanes as well as the oxidation of CO. I will
discuss characteristics of the binding and activation of alkane σ-complexes on
PdO(101) as determined from both experiment and density functional theory
calculations. I will also discuss elementary processes involved in the oxidation of CO
and other small molecules on PdO(101).

COLL 362

Imaging the dynamics of water molecules on RuO$_2$(110)

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RuO$_2$ has a wide range of applications in photocatalytic water splitting, heterogeneous
catalysis, electrochemistry and many other energy-related areas. Here, we prepared
stoichiometric, reduced and oxidized RuO$_2$(110) surfaces and studied water adsorption,
dissociation, and diffusion using time-lapsed scanning tunneling microscopy. On
stoichiometric RuO$_2$(110) we show that water monomers adsorb on top of the Ru sites
and are immobile below ~223 K. At temperatures above 238 K, the monomers are
found to diffuse along Ru rows and form water dimers, trimers and tetramers with
dimers being the most stable configuration. The onset for dimer diffusion is observed at
~ 277 K indicating higher diffusion barrier than that for monomers. The diffusion barrier
for water dimers is determined to be ~0.73 eV, which is significantly higher compared to
0.35 eV determined previously on the isostructural TiO$_2$(110).$^{1}$ On reduced RuO$_2$(110),
we find that water molecules dissociate in bridging oxygen vacancies forming pairs of
bridging hydroxyls. Subsequently, both the along- and across-row diffusion of proton is
observed at room temperature. On oxidized RuO$_2$(110), water molecules react with
oxygen adatoms on Ru rows and form pairs of terminal hydroxyl groups that can
reversibly dissociate back to water and adatom. Along- and across-row diffusion of
water molecules at room temperature is tracked by following the position of hydroxyl
pairs.

$^{1}$ J. Matthiesen, J. Hansen, S. Wendt, E. Lira, R. Schaub, E. Lægsgaard, F.

COLL 363

Reaction pathway analysis of methanol synthesis from CO$_2$ hydrogenation over
in$_2$O$_3$-based catalysts

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Catalytic conversion of CO$_2$ into liquid fuels and other value-added chemicals is a
promising alternative to controlling CO$_2$ emission. Developing highly selective catalysts
for CO₂ conversion becomes a focused research area in catalysis. Key to many catalytic CO₂ conversion processes is the adsorption of CO₂ on the surface of the catalysts. In this talk, I will discuss our DFT computational results on the activated CO₂ adsorption on a number of oxide surfaces. I will then present the reaction pathways for CO₂ hydrogenation to methanol on the In₂O₃(110) surface and a model Pd/In₂O₃ catalyst, along with the preliminary experimental studies that tested some of the theoretical predictions.

**COLL 364**

**Interfacing biology with synthetic matrices**

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Our research lies at the interface of materials and biology. We are interested in developing intelligent biomaterials that closely mimic the molecular composition, biological functions, mechanical responsiveness and multiscale organizations of the natural extracellular matrices. These synthetic matrices are constructed using diverse and modular building blocks employing highly efficient bio-orthogonal coupling chemistries in conjunction with concerted supramolecular interactions. Examples of these materials are hyaluronic acid-based microgels and doubly crosslinked networks, mechano-responsive hydrogels crosslinked by block copolymer micelles and peptide/polymer multiblock hybrid copolymers. These materials, combined with defined mechanical cues and biological factors, create a three dimensional microenvironment for improved understanding of cell biology. Using biologically inspired paradigms, we are developing methodologies for the engineering of healthy, replacement tissues such as cartilage, vocal folds and salivary glands, as well as disease models, such as prostate cancer tumor spheroids.

**COLL 365**

**Time-dependent migratory behaviors in the long-term studies of fibroblast durotaxis on a hydrogel substrate fabricated with a soft band**

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Durotaxis, biased cell movement up a stiffness gradient on culture substrates, is one of the useful taxis behaviors for manipulating cell migration on engineered biomaterial surfaces. In this study, long-term durotaxis was investigated on gelatinous substrates containing a soft band of 20 µm, 50 µm, and 150 µm in width fabricated using photolithographic elasticity patterning; sharp elasticity boundaries with a gradient strength of 300 kPa/50 µm were achieved. Time-dependent migratory behaviors of 3T3
fibroblast cells were observed during a time period of three days. During the first day, most of the cells were strongly repelled by the soft band independent of band width, exhibiting the typical durotaxis behavior. However, the repellency by the soft band diminished and more cells crossed the soft band or exhibited other mixed migratory behaviors during the course of the observation. It was found that durotaxis strength is weakened on the substrate with the narrowest soft band and that adherent affinity-induced entrapment becomes apparent on the widest soft band over time. Factors, such as changes in surface topography, elasticity, and/or chemistry, likely contributing to the diminishing durotaxis during the extended culture were examined. Immunofluorescence analysis indicated preferential collagen deposition onto the soft band, which is derived from secretion by fibroblast cells, resulting in the increasing contribution of haptotaxis toward the soft band over time. The deposited collagen did not affect surface topography or surface elasticity, but did change surface chemistry, especially on the soft band. The observed time-dependent durotaxis behaviors are the result of the mixed mechanical and chemical cues. In the studies and applications of cell migratory behavior under a controlled stimulus, it is important to thoroughly examine other (hidden) compounding stimuli in order to be able to accurately interpret data and to design suitable biomaterials to manipulate cell migration.

COLL 366

**Functionalized polymeric surfaces generated by electron beam lithography for applications from encrypic messages to enhanced cell adhesion**

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Polymers are readily micro- and nanopatterned onto surfaces using electron beam (e-beam) lithography, which cross-linked the chains to the surface. We exploit this to prepare functionalized surfaces that can be used to immobilize proteins. For example, if poly(ethylene glycol) with functional end groups are utilized, then proteins are readily immobilized on the resulting surface-bound hydrogels. Since conjugating proteins on surfaces in specific orientations is important for retention of bioactivity, initially, poly(ethylene glycol)s (PEGs) were synthesized with biotin, aminooxy, maleimide, and nitritriacetic acid (NTA) end groups. As a result, proteins conjugated to the surface features via ligand binding sites, N-terminal o xoamides, free cysteines, and histidine tags, respectively. Patterns of different proteins side by side and in three-dimensional arrangements are readily made. We also can pattern oligo(ethylene glycol) methacrylate-based thermoresponsive polymers with amine end-groups. The lower critical solution temperatures (LCSTs) of the polymers were readily adjusted by altering the length of oligo(ethylene glycol) side chains or by changing the ratio of monomers with different lengths. The polymers were patterned on silicon surfaces by electron beam lithography, followed by the conjugation of self-quenching fluorophores to the patterned hydrogels utilizing the amine end-groups. At room temperature, the hydrogels were brightly fluorescent in water. Upon increasing the temperature to values above the volume phase transition temperature (VPTT) of the respective gel, a dramatic decrease
in the fluorescence intensity was observed due to self-quenching of fluorophores in the collapsed state of the gel. Importantly, the temperature-induced fluorescence switch was reversible. In this way, we generated morphing structures that reversibly display different messages at different temperatures. Fabrication of the surfaces and application in enzyme cascades, cell adhesion, and encryptic messages will be discussed.

COLL 367

Materials and methods for studying the drug-delivery of microcarriers across the apical barrier of reconstituted 3D epithelial tissues

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In vitro cell-culture techniques attempt to recreate biological architectures in order to test drugs, study cellular mechanisms, or reconstitute functional tissues. Several challenges associated with recapitulating the physical and chemical cues that tissues experience in vivo still need to be resolved. To overcome the limitations of current methods used to pattern spatially and geometrically resolved multicellular three-dimensional (3D) tissues in very soft biomimetic hydrogels, we use sacrificial scaffolds to temporarily accommodate cell-aggregates in 3D before transferring them to a reconstituted extracellular matrix (ECM). We have already shown that (1) this sacrificial micromolding approach promotes cyst-formation and proper polarization of established epithelial cell lines, (2) our methods allow us to quantify the localization of cytoskeletal filaments within a reconstituted tissue as a function of time, and (3) we can control the lumenization of epithelial cells as a function of tissue size. Herein, we present the potential of this technique for studying the interactions of 3D tissues with foreign objects like drugs or drug-carriers in a physiologically relevant microenvironment. To the best of our knowledge, this is the first work that describes the non-intrusive localization of microcarriers within the lumen of an intestinal cyst in vitro (Figure 1). We use this method to investigate the effect of different micro- and nano-topographies on drug-delivery across epithelial barriers in 3D.
We report the synthesis of a new cysteine-based methacrylic monomer (CysMA) by selective thia-Michael addition of a commercially-available methacrylate-acrylate precursor in aqueous solution with recourse to protecting group chemistry. Poly(cysteine methacrylate) (PCysMA) brushes were from the surface of planar silicon wafers by surface initiated atom-transfer radical polymerisation. The kinetics of brush growth were investigated. Brush thicknesses of ca. 27 nm were achieved within 270 min. at 20°C. Each CysMA residue comprises a primary amine and a carboxylic acid, hence the resulting PCysMA brushes exhibit either cationic, zwitterionic or anionic character depending on the solution pH. The pH-responsive behavior of photopatterned brushes was studied by atomic force microscopy. Surface zeta potential studies confirm that PCysMA brushes are highly extended either below pH 2 or above pH 9.5, since they possess either cationic or anionic character, respectively. However, at intermediate pH, PCysMA brushes acquire zwitterionic character and exhibit excellent anti-biofouling properties at around physiological pH, with essentially no cytotoxicity being observed.
On exposure to UV radiation, PCysMA brushes undergo photodegradation: AFM topographical imaging indicates significant mass loss from the brush layer, while XPS studies confirm that exposure to UV radiation produces surface aldehyde sites that can be derivatized subsequently with amines. UV exposure through a photomask yielded sharp, well-defined micro-patterned PCysMA brushes. Nano-patterned PCysMA brushes were fabricated using interference lithography (IL). Selective adsorption of green fluorescent protein (GFP) onto patterned PCysMA brushes was examined using confocal fluorescence microscopy and AFM. Unexposed PCysMA brushes proved to be highly protein-resistant, whereas protein conjugation to surface aldehyde groups occurred in the exposed regions. Finally, PCysMA undergoes complex base-catalyzed degradation in alkaline solution, leading to the elimination of several small molecules. However, good chemical stability was observed when PCysMA brushes were immersed in aqueous solution at physiological pH.

COLL 369

Compliant polymeric scaffolds with nanofabricated membranes for improved pancreatic islet function and viability

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In the pancreas, islets are surrounded by a complex microenvironment that is not recapitulated during islet transplantation, resulting in limited islet function. Creating a proper microenvironment to support islet secretory function within an encapsulation device that protects the cells from the surrounding immune response is crucial for the success of this approach. To achieve this goal, we are developing: (1) a polyacrylamide (PA) islet microenvironment to better understand the microenvironment necessary to maintain islet function and (2) a nano-porous thin-film polycaprolactone (PCL) macro-encapsulation device that protects the islets from immune destruction.

PA micro-well scaffolds at 0.1 kPa and 10 kPa were fabricated using standard photolithography to create 3D cell clusters from dissociated islets and beta cells. We show a significant stiffness-dependent increase in the glucose stimulated insulin response per cell for 3D beta cell clusters grown on 0.1kPa scaffolds in comparison to 10kPa scaffolds. Our data suggests that the physical interactions with the microenvironment regulate insulin processing through the MLCK and ROCK mechanosensing pathways. Furthermore, our data suggests active beta-catenin signaling is requires for stiffness dependent insulin regulation. To improve long-term in vivo islet viability we fabricated a thin-film device from PCL, a biodegradable polymer approved by the FDA for biomedical devices. In vitro the device demonstrates unhindered insulin kinetics. In vivo the device vascularizes and protects against allo-
rejection, this suggests thin-film devices engraft and maintain alloimunity after a period of one month. Since our devices demonstrate cell viability at one-month, we predict that alloimunity can be maintained indefinitely. By understanding the role of microenvironment and designing a device that promotes improved islet function, viability and immune protection, we can better design the therapeutics necessary to treat diabetes.

**COLL 370**

**Reversible self-assembly of α-synuclein peptide on gold colloidal nanoparticles' surfaces**

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The insoluble fiber formation of the α-synuclein peptide is regarded as a major pathological hallmark of Parkinson's disease. The mechanism of fiber formation is speculated to involve an intermediate oligomers, and the detailed investigation of the oligomers has been challenging. We made an approach to stably conform the oligomeric forms by using the surface potential of a nanoparticle, and observed a reversible self-assembly over 60 nm gold colloid through a repetitive change of pH between pH4 and pH 10. We concluded that an α-synuclein monomer forms an unfolded conformation at pH 4 and re-assembled to a folded conformation at pH 10, repetitively. The smaller size than 60 nm did not exhibit any signs of this reversible self-assembly, and it implies that there is a threshold surface area at over that value, enough surface potential to support stable oligomers.

**COLL 371**

**Effect of polyelectrolyte multilayer deposition conditions on growth factor release and preosteoblast behavior**

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The goal of this work is the controlled long term release of bone morphogenetic protein 2 (BMP-2) from polyelectrolyte multilayer coatings so as to improve osseointegration and durability of titanium implants. Polyelectrolyte multilayer coatings were prepared from solutions of poly(methacrylic acid) and poly-L-histidine. BMP-2 was adsorbed to the surface of anodized titanium and polyelectrolyte multilayer coatings were built up on top of the BMP-2. The effect of deposition conditions on coating properties and BMP-2 release, as well as preosteoblast response to these parameters, was investigated.
Polyelectrolyte multilayers prepared under natural conditions to those prepared from solutions at an acidic pH and solutions containing salt. High levels of BMP-2 release were achieved. Enhanced preosteoblast differentiation was observed on coatings prepared from modified solutions; however, this increased differentiation was apparent for both BMP-2-eluting and control coatings. Additionally, a positive relationship between surface roughness and differentiation was observed, which may account for increased differentiation for systems that do not release BMP-2. The effects of both BMP-2 release and surface roughness on preosteoblast response are investigated and proposed methods of adjusting these properties independently will be explored.

**COLL 372**

**Molecular catalysis science, nanoparticle synthesis, and instrument development for characterization under reaction conditions: Conquering catalytic complexity**

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Most heterogeneous, homogeneous and enzyme catalysts are nanoparticles. Colloid synthetic techniques of monodisperesed metal nanoparticles in the 0.8 – 10 nm range with precise size distribution indicate that most catalytic reactions to be structure sensitive. Monometallic and bimetallic nanoparticles as well as core-shell structures with oxide shell and metal core are used to study multipath catalytic reactions with high product selectivity. It was found that the size and shape of metal nanoparticles control catalytic reaction rates and selectivities. In order to explore reasons of size and shape control high pressure in-situ surface techniques that include sum frequency generation vibrational spectroscopy, high pressure scanning tunneling microscopy and well-controlled oxide metal interfaces along with synchrotron techniques of X-ray spectroscopies are utilized under reaction conditions. Using these techniques, reaction intermediates, changes of surface composition of bimetallic catalysts under reducing and oxidizing conditions and mobility of reactants and surface structure using high pressure scanning tunneling microscopy were explored and determined. Small nanoparticles, below 2 nm range, were found to have changes of electronic structure that give rise to high oxidation state clusters under reaction conditions. These were utilized to heterogenize homogeneous catalysis using metal nanoclusters in the range of 40 atoms or less to carry out homogeneous catalytic reactions on heterogenized surfaces. Oxide metal interfaces were found to be Lewis acid to selectively control chemistry at very high turnover rates. Hydrogen and carbon monoxide catalytic oxidation generates a steady electron flow across platinum–titanium Schottky diodes. The thin metal film (about 4 nm) provides hot electrons that render the oxide metal interfaces active reaction sites. Nanocrystal bilayers carry out tandem catalysis using cerium oxide, platinum, silica sandwiches to produce combined methanol decomposition and hydroformylation chemistry instead of hydrogenation. In the future construction of catalyst architecture to increase selectivity of multipath reactions should
be explored to carry out primary and secondary product reactions similar to enzyme catalytic processes.

**COLL 373**

**Adsorption induced autoamplification of enantiomeric excess**

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One of the key experimental challenges in the study of enantioselective surface chemistry is the development of tools or methods that can distinguish one enantiomer from the other. For two reasons we have identified aspartic acid \((\text{HO}_2\text{CCH(NH}_2\text{)CH}_2\text{CO}_2\text{H})\) as an ideal chiral probe for studying enantioselective surface chemistry on naturally chiral Cu single crystal surfaces. Firstly, it exhibits extremely highly enantiospecific surface reaction rates because of the fact that it decomposes by an explosive mechanism with highly non-linear kinetics. Secondly, it is an amino acid and as a consequence we are able to use \(^*\text{L-aspartic acid-1,4-}^{13}\text{C}_2\) \((^*\text{L-Asp})\) which can be distinguished from D-aspartic acid (D-Asp) using mass spectrometry. These have been studied on the achiral Cu(110) and chiral Cu\((3,1,17)\)^R&S surfaces. Decomposition of Asp on the Cu(110) and chiral Cu\((3,1,17)^\text{R&S}\) surfaces yields CO\(_2\) and CH\(_3\)-C\(^{\circ}\)N as primary products. Not surprisingly, \(^{13}\text{C}\) labeling in \(^*\text{L-aspartic acid-1,4-}^{13}\text{C}_2\) show that the \(^{13}\text{CO}_2\) comes only from the carboxylate end-groups while labeling of other atoms shows that the CH\(_3\)-C\(^{\circ}\)N product arises only form the C2 and C3 carbon atoms. Exposure of a racemic mixtures of \(^*\text{L-Asp}^{}\) and D-Asp has been used to establish enantiospecific adsorption equilibria on the Cu\((3,1,17)^\text{R&S}\) surfaces. During exposure to the racemic mixture, the enantiomer with the higher binding energy is capable of displacing the more weakly bound enantiomer to establish a non-racemic adsorbed layer. In other words, exposure of the Cu\((3,1,17)^\text{R&S}\) surfaces to the racemic mixture in the gas phase results in a separation and enrichment of one of the two enantiomers on the surface. Recently we have shown that even the exposure of non-racemic mixtures of D- and \(^*\text{L-Asp}^{}\) to achiral Cu(111) surface can lead to amplification of enantiomeric excess on the surface. This can arise from the formation of homochiral clusters on the surface and can be modelled using a non-linear Langmuir-like isotherm that accounts for cluster formation.

**COLL 374**

**Towards molecular electronics: Using solution-based methods to deposit nano-objects**

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Nanoscale one-dimensional materials, commonly called nanowires, have properties that differ significantly from their bulk counterpart materials, and thus have applications in
areas including sensing, energy conversion, electronics and optoelectronics. One of the major challenges in the practical use of nanowires is their integration into complex functional structures in a predictable and controlled way. We have recently introduced two promising new techniques by which to direct the in situ growth of metallic and semiconducting nanowires. ENDOM, or Electroless Nanowire Deposition On Micropatterned substrates, employs electroless deposition (ELD) to form metallic nanowires on substrates. We illustrate ENDOM by deposition of Ni, Cu, Pd and other nanowires on patterned –OH/–CH₃ SAMs. SENDOM, or Semiconductor Nanowire Deposition on Micropatterned surfaces, uses chemical bath deposition (CBD) to deposit semiconductor nanowires. We demonstrate SENDOM by deposition of CuₓS nanowires on patterned –COOH/–CH₃ SAMs. Fundamental to the optimization and application of these methods is an understanding of the interaction of reactants with the terminal functional groups of organic thin films. These interactions significantly affect transport and reaction rates, the control of which is critical in optimizing ENDOM and SENDOM and their extension to different nanowire materials and substrates.

COLL 375

Catalytic model systems studied by high-resolution, video-rate Scanning Tunneling Microscopy

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For decades single-crystal surfaces have been studied under ultra-high vacuum (UHV) conditions as model systems for elementary surface processes. This “surface science approach” has contributed substantially to our understanding of the processes involved in especially catalysis.

In this talk I will show how STM can reveal fundamental processes in relation to catalysis, and how we can extract quantitative information on surface diffusion of adatoms and molecules. We use time-resolved, high-resolution STM images/movies to understand diffusion of vacancies, interstitials and molecules, e.g. water molecules on oxide surfaces, sintering and diffusion of nanoclusters on oxide surfaces, diffusion of intermediate species, and to identify active sites and to determine new nanostructures with novel catalytic properties (see www.phys.au.dk/spm). The atomic-scale information obtained may even lead to the design of new and improved catalysts in certain cases.

COLL 376

Influence of defect sites on elementary surface reactions in Fe-based FTS: Insights from DFT

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The Fischer-Tropsch synthesis (FTS) reaction converts synthesis gas derived from coal, natural gas, or biomass into chemicals and hydrocarbon fuels. Atomic-level insight into the mechanism of FTS can potentially lead to a predictive understanding of changes in catalyst behaviour as a function of operating conditions. Density functional theory is well suited to investigating surface reaction mechanisms, but its application to industrial FTS remains challenging, due in part to the complexity of the catalysts employed. In Fe-FTS, iron carbides form under FTS conditions, of which $\chi$-Fe$_5$C$_2$ has been associated with FTS activity. In this work, we present a systematic investigation of early steps in Fe-FTS as a function of $\chi$-Fe$_5$C$_2$ surface structure[1,2], incorporating carbon vacancy and step sites to investigate direct and hydrogen-assisted dissociation of adsorbed CO, as well as subsequent C and O removal.

Although the strength of CO adsorption was found to be largely insensitive to the nature of the adsorption site, significant differences in the degree of activation of the C–O bond were found, with adsorption at step sites facilitating a higher degree of coordination of CO to the surface, with a correspondingly larger increase in the C–O bond length and red-shift in the C–O stretching frequency relative to adsorption in terrace sites. The more activated CO adsorbed at step vacancy sites is associated with a significantly lower activation energy for direct dissociation. In the terrace environment, direct and hydrogen-assisted paths have comparable overall activation energies, and can be kinetically competitive depending on the surface concentration of hydrogen and empty sites. In contrast, for step sites the hydrogen-assisted route is less favourable than direct dissociation. Overall, C and O removal are strongly endothermic in the calculated coverage regime, suggesting that coverage effects will play a decisive role in determining surface reaction energetics under FTS conditions.


**COLL 377**

**Formation of small hydrocarbon molecules from hydrogenated graphene**

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Abundance of atoms in the interstellar medium is well understood in terms of nuclear reactions taking place inside stars, their masses and their evolution. In contrast, the existence of clouds of small molecules in space is still an unexplained puzzle. An example is the H$_2$ molecule. It cannot be formed in the typical temperature and vacuum conditions to be found in the interstellar medium without the help of other intervening systems (i.e., dust grains), but it is readily observed.
In this talk we shall review enthalpies of formation and barriers computed with ab-initio Density Functional Theory to obtain small organic molecules from dust carbonaceous surfaces. Preliminary simulations show that atomic Hydrogen, an abundant element in space, lowers considerably barriers to extract from graphene a number of small organic molecules like C2H2, C2H4, CH4, C6H6, etc. We are currently exploring these rates in order to assess whether this might be a possible explanation to the detection of these products in the interstellar medium.

 COLL 378

Structure of amino acid overlayers at symmetric and chiral Cu surfaces

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Chirality at solid surfaces has become a major topic within surface science. A low-index surface of an fcc metal such as Cu has mirror symmetry, but chirality can be imposed upon it by adsorbing a 'chiral modifier' species. Alternatively, an 'intrinsically chiral' surface can be created simply by orienting the surface such that it is devoid of all bulk mirror symmetry. Understanding forms of symmetry reduction and their implications is of fundamental scientific interest; in addition, chiral surfaces may have great potential for important practical applications. One example is enantioselective heterogeneous catalysis for the pharmaceutical industry: can a chiral surface steer a reaction towards an enantiopure product? Another is sensors: does a chiral surface show a measurably different physical response to the two enantiomers of a chiral adsorbate?

A detailed knowledge of the ways that chirality can manifest itself at surfaces is essential to developing insight into how surface chirality might be exploited. In this talk, I shall discuss our work in Cambridge exploring amino acid overlayers on Cu surfaces as model chiral systems. Through a combination of rigorous experimental and theoretical surface science techniques, we are systematically investigating the relationships between molecular chirality, footprint chirality and lattice chirality. We are focussing particularly on the role of substrate symmetry by investigating Cu{311}, which has a single mirror line, and Cu{531}, which is an intrinsically chiral surface, as substrates. I will outline the insights that we have gained so far, and the further questions that are raised by our observations.

 COLL 379

Ionic liquids behave as dilute electrolyte solutions

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Since ionic liquids (ILs) are composed solely of ions, dilute electrolyte theory is typically presumed to be inapplicable for modeling their electrostatic screening properties. Using a recently developed “electrochemical surface forces apparatus” we carried out direct force measurements between two charged surfaces across the common IL [C4mim][NTf2]. Our results show an exponentially decaying force consistent with the formation of a diffuse electric double-layer, where the characteristic decay (Debye) length is in quantitative agreement with a simple thermodynamic model with only a small fraction of the IL ions thermally dissociating to behave as effectively free ions, while the remaining ions behave as a highly correlated dielectric medium. Thus, outside of strongly surface bound ion layers, ILs can be conceptualized as dilute electrolyte solutions in confined interfaces, and probably also in the bulk (see figure). Our results [1] resolve several scientific paradoxes concerning ILs, and provide a general, molecular-scale framework that may guide the design of high or ultra-low conductivity ILs for energy storage applications.

Ionic liquids at electrochemical interfaces

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The interface between an electrode and a molten salt or ionic liquid is particularly topical - since the use of ionic liquids in electrochemical technologies is expanding rapidly. Macroscopic (current/voltage) data on such systems is often analysed by appeal to classical double-layer ideas yet the validity of these mean-field concepts, introduced to describe dilute electrolyte solutions, is undermined by the molecular scale information arising from novel types of experiment. New insights, linking the macroscopic and microscopic observations, arise from atomistic computer simulations, where strong correlation effects arising from the coulombic and short-range interactions between the ions and with the electrode surface are included, and also from emerging theories, in which the mean-field treatment is systematically extended. A major challenge for simulation is to treat the interface and the interionic interactions at a sufficiently realistic level that the calculated quantities may be compared with the results of experiments on real materials. The methods underpinning recent simulations of electrochemical “double layer” capacitors (supercapacitors) will be described. Supercapacitors store energy at the electrolyte/electrode interface through reversible ion adsorption leading to higher charge/discharge rates and better cyclability compared to batteries; very high capacitances are achieved using porous electrodes [1]. The nature of the reorganisation of the molecular organisation at the interface in response to an applied potential is best studied at a planar interface, where simulation and experimental observation may be directly compared [2]. Recent work shows a link between peaks observed in the variation of the differential capacitance with potential and abrupt structural transitions resembling phase transitions.


Local structure and dynamics in mixtures of benzene and ionic liquids

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OKE spectra of ionic liquids and their mixtures with benzene and other molecules have been obtained recently by Quitevis and his co-workers. Although it would be difficult to simulate the spectra directly, the Fourier transforms of velocity autocorrelation functions provide a good proxy. These allow one to determine contributions from different species
and their translational and librational motions. I present spectra from 1:1 mixtures of benzene and [mmim][Ntf2] (dimethyl imidazolium \([N(SO_2CF_3)_2]\)) and relate them to the local structure in the liquid. I compare the 1:1 mixture to the neat liquids of benzene and the ionic liquid and to the pure ionic liquid benzylmethylimidazolium with the same anion.

COLL 382

Ion pairing and hydrogen bonding in ionic liquids

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Ionic liquids (ILs) are liquids composed entirely of ions. \([1]\) Within the liquid the lack of single cation-anion associations, thus, the lack of "ion pairing" was suggested, \([2]\) or at least a certain ion pairing deficiency due to structural mixture of ion-pairing with non-associative behavior, i.e. scale of ionicity,\([3]\) as opposed to the vapor structure consisting of solely ion pairs. \([4]\) Thus, depending on the definition of the term "ion pair" - especially in terms of time scales [2, 5] - the situations in which ion pairing might occur or can be fabricated may also alter. The importance of hydrogen or intermediate bonding in ionic liquids (ILs) has been recognized.\([5]\) However, the term hydrogen bonding has to be treated with care, because depending on the kind of IL different intermediate interactions between cations and anions occur. In this presentation we discuss ion pairs in ionic liquids, and show different examples of changes in the structure or of the persistence. Furthermore, we show examples where hydrogen bonding in ionic liquids and even proton transfer takes place.\([6]\) Mainly, we present mixtures of ILs, and \(CO_2\) absorbed in ILs. \([6,7]\) We discuss interface and gas-phase conditions \([8]\) and consider also a solute ion pair in ionic liquids \([9]\).


Unusual charging behavior of ionic-liquid electric double layers

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The kinetics of electric double layers (EDL) is closely related to the performance of a wide variety of nanostructured devices including supercapacitors, electroactuators, and electrolyte-gated transistors. While EDL formation in aqueous electrolytes has been well understood, relatively little is known on the kinetics of ionic liquid EDLs pertinent to these modern applications. In this work, we use a classical time-dependent density functional theory to study the charging behavior of a model ionic liquid EDL system that captures the essential kinetic properties. By examining the variations of the ionic density profiles and the surface charging density in response to a sudden increase of the electrode voltage, we observe that, at certain conditions, the energy density shows a rapid increase only at the initial stage of charging and decays as the system reaches equilibrium. The nonmonotonic charging behavior can be explained in terms of the long-range layering structure of ionic liquids and the oscillatory variation of the capacitance with the system geometry.

Molecular reorientation in fluids resulting from thermal gradients

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Thermomolecular orientation (TMO) refers to the effect of a thermal gradient on the orientation of an asymmetric molecule (Römer et al., Phys. Rev. Lett. 108, 105901), leading to significant electric polarization in the case of polar fluids such as water (Armstrong et al., J. Chem. Phys. 140, 016102). In this presentation I will report on our continuing work in elucidating the details of the TMO effect via non-equilibrium molecular dynamics simulations of simple model fluids, as well as our progress in predicting the spectroscopic signature(s) of the TMO effect, and prospects for actual experimental observation of the effect, which has heretofore only been seen in computer simulations.

**COLL 385**

**Single molecule spectroscopy of nanoparticle - protein interactions**

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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. Furthermore, single molecule fluorescence spectroscopy of dye-labeled proteins reveals the time scales of protein binding and unbinding to individual plasmonic nanoparticles. Localization of individual binding events allows us to resolve protein binding dynamics with resolution beyond the diffraction limit.

**COLL 386**

**Using analytical tools to assess binding between nanomaterials and proteins**

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With the rapid advancement of nanotechnology, engineered nanoparticles (NPs) have found enormous applications in diverse areas including molecular sensing, energy production, biomedical imaging, and drug delivery. On the other hand, the increasing production of NPs augments their release to the environment and raises great safety concerns. Both trends call for more profound understanding of how NPs interact with
biosystems to ensure effective and safe employment of NPs. Since such interactions are in fact mediated by the biomolecules, especially proteins, adsorbed on the NPs once they enter the biosystem, our group has been utilizing various analytical technologies to study NP-protein interaction. We developed a capillary electrophoresis-based method to measure the binding affinity, which offers fast running speed, high resolution power, and non-destructive separation of the nanoparticle-protein complex. We also employed mass spectrometry (MS) coupled with the crosslinking chemistry to identify the binding epitope of the Fe₃O₄ NPs on human serum albumin. Furthermore, we developed a field-flow fractionation-based technique to help study the dynamic feature of protein adsorption on NPs. Currently, we utilized two isolation methods to study protein corona formed outside of NPs carrying drug molecules, trying to elucidate the roles of nanocarriers for improved drug efficacy. With all these analytical tools developed in our group, we can systematically study the dependence of protein affinity, binding consequence, and corona formation on the physicochemical properties of NPs, gaining more knowledge about the interaction driving force and possible consequences.

**COLL 387**

**Activation of thiols on metallic nanoparticles and its effect on the particle optical properties**

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Adsorption of a variety of thiol molecules has been widely used to affect the optical properties of metallic nanoparticles (MNPs) and enable new technological capabilities in applications spanning from biosensors to photonics. A fundamental understanding of the adsorption/reaction processes of thiols on the MNP surfaces and how thiol adsorption affects the MNP optical properties is critical to the technology development. In this talk we discuss 1) how nonlinear (second harmonic) light scattering can be used to probe the reaction of thiols on the surface of MNPs, 2) how thiol structure and MNP surface treatment may affect thiol reaction/adsorption, 3) how layering of different thiol molecules may affect the MNP plasmonic structure, and 4) how thiol adsorption can be used to dramatically increase the fluorescence quantum efficiency (in some cases by more than two orders of magnitude) of the MNPs.

**COLL 388**

**Molecular interactions at colloidal/water interfaces**

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SHG studies of the adsorption of the HIV-1 peptide to neutral and charged membrane mimetic phospholipid liposomes will be presented. The adsorption free energy, the electrostatic potential which is not based on the Gouy-Chapman model, and the number of peptides adsorbed have been determined. A comparison of the electrostatic potential
obtained from SHG measurements with the zeta potential obtained from electrophoresis measurements is given. SHG results of acid – base equilibria at a colloidal polymer microparticle/aqueous interface are discussed.

**COLL 389**

Interaction of functionalized gold and diamond nanoparticles with supported lipid bilayers

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Lipid membranes are the doorway from the environment to the interior of cells. The molecular level interactions that govern nanoparticle (NP) uptake by cells are not completely understood, but a deeper understanding of these interactions has the potential to improve a wide range of scientific fields. At present, only limited molecular scale information is available on the interactions of NPs with cellular membranes that influence their attachment to and internalization by cells. We investigated NP interaction with model phospholipid membranes by varying both the chemistry of prepared supported lipid bilayers and of the functionalized NPs. Bilayer properties examined included membrane fluidity and headgroups expressed to solution. The nanoparticles employed varied in core composition (gold or diamond) and surface functionalization. We employed a suite of techniques to investigate NP interaction with the supported lipid bilayers including quartz crystal microbalance with dissipation, fluorescence microscopy, atomic force microscopy, and nonlinear optical spectroscopies. Surprisingly, positively charged functionalized NPs attached to supported lipid bilayers in a manner that was not consistent with electrostatic forces being the dominant force involved.

**COLL 390**

Diffusing colloidal probes of cell surfaces

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To engineer nanoparticles for novel biosensing, diagnostic imaging, and drug delivery applications, the interactions of nanoparticles with the surface of cells must be
characterized to better understand their influence on specific and non-specific cell surface adhesion, internalization pathways, and toxicity. In order to develop models to aid in optimization and design in these systems, direct measurements of colloidal interactions with cell surfaces are required that are both quantitative and sensitive to determine the impact of particle composition and surface chemistry. In this talk, we report the use of diffusing colloidal probes to directly measure cell surface interactions with kT-scale sensitivity with newly developed imaging and analysis techniques. Dark field video microscopy allows for label-free imaging of colloidal particles and live cells. With combined real-time particle tracking and cell boundary determination, particle trajectories can be monitored in relation to their distance from the cell surface which allows for direct measurement of equilibrium and non-equilibrium colloid-cell interactions. Using this technique, polymer, protein, and carbohydrate functionalized colloidal silica were used to measure specific and non-specific macromolecular interactions with the surface of epithelial breast cancer cells. Ultimately, our results demonstrate how diffusing colloidal probe microscopy can be used to characterize biomolecular and biophysical properties of cell surfaces.

COLL 391

X-ray triggered release of drugs from nanoscale drug carriers

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We have devised a series of nanoscale cancer drug carriers that can release the stored drug molecules upon irradiation of hard X-rays in water and cells. Such release can reduce the dose of X-rays needed to kill cancer cells. A number of mechanisms have been created to allow efficient release of drugs and reduction of the X-ray dose.

COLL 392

Nitric oxide-releasing dual-action dendrimer biocides for biofilm eradication

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The increasing prevalence of antibiotic-resistant bacteria in clinical settings has led to biofilm-based infections that display a pronounced resistance to antibiotics, necessitating the development of new, more effective therapeutics. Combining two mechanistically different antibacterial agents (e.g., non-depleting biocide with releasable agent) on a single scaffold represents a promising strategy for increasing bactericidal efficacy while offsetting the development of resistance. Herein, we describe the synthesis of alkyl chain-modified dendrimers as contact-based biocides by tethering epoxides of varying alkyl chain length (i.e., butyl, hexyl, octyl, and dodecyl) to the dendrimer exterior. The dendrimers are further modified with N-diazeniumdiolate NO
donors to yield NO-releasing dual-action dendrimer biocides. We evaluate the efficacy of these dendrimer biocides against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and methicillin-resistant *Staphylococcus aureus* biofilms as a function of alkyl chain length and dendrimer generation. Fluorescent confocal microscopy is used to visualize dendrimer-bacteria association, intracellular NO accumulation, and bacterial cell death. These studies demonstrate the potential to tune macromolecular scaffolds for optimal biofilm eradication.

**COLL 393**

Mixed chain-length lipid bilayer for improved incorporation of sterically bulky hydrophobic drugs in liposomal nanoparticles

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Nanoparticles have opened up many exciting opportunities to deliver therapeutics more effectively and enhance the efficacy thereof, to treat diseases such as cancer. Lipid nanoparticles, now widely employed as drug delivery systems clinically, have revolutionized the pharmacokinetics, tissue distribution, bioavailability, and toxicity profile of small molecule chemotherapy agents, such as doxorubicin. The mechanism of hydrophobic drug binding to the lipid membrane of liposomes, however, has not been thoroughly studied. For that reason, liposomal therapeutics in clinical applications have been generally limited to mostly-planar or hydrophilic compounds. In this presentation, we wish to discuss our recent findings of how sterically bulky organic molecules interact with the lipid bilayers. We employ a novel Artemisinin dimer derivative as the model drug in a mixture of two saturated lipids of different carbon chain length to achieve optimized drug-in-liposome stability and drug incorporation efficiency. The Artemisinin dimer liposomal nanoparticle formulation showed promising efficacy and selectivity against human breast cancer cells in vitro. This investigation highlights the importance of considering the geometry of the hydrophobic molecule when designing a liposomal system. With an appropriate pre-installed hydrophobic cavity obtained by using a mixture of lipids with different fatty acid chain length in membrane, we demonstrate the improved stability of formulation in presence of serum with.

**COLL 394**

Cornell dots as a new class of fluorescent nanoparticles to improve visualization in cancer surgery

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Despite significant promise of nanomaterials in medicine, few colloidal materials make the transition into the realm of clinical applications. In this presentation a novel class of multifunctional fluorescent silica-based core-shell nanoparticles will be introduced referred to as “Cornell dots” or simply “C dots”. These particles have sizes below 10 nm, which is below the threshold for renal clearance, leading to favorable biodistributions. These smaller than 10 nm sized PEGylated labels for nanomedicine are the first dual-modality (optical/PET) hybrid nanoparticles of its class and properties receiving investigational new drug (IND) FDA approval for first in-human trials in the US. In this presentation, after shortly reviewing results on C dot synthesis, characterization, optical properties and animal studies, first results will be reported on clinical trials with human melanoma patients assessing particle safety. Subsequently work towards employing these probes in sentinel lymph node mapping will be described in which a specific camera system was developed that surgeons can use for visualization of nodes during surgery. These efforts recently also lead to FDA IND approval for a new clinical trial now open for patient recruitment.

References:


COLL 395

Polymer colloids for the controlled elease of heparin binding growth factors

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The delivery of growth factors is important in regenerative therapies. These medium molar mass proteins are the key signalling molecules that initiate and control the production of viable tissue. In vivo many growth factors bind to the negatively charged glycosaminoglycan heparin and we consider that other charged polymers could perform the same function. With this in mind, core-shell particles have been prepared by surfactant-free emulsion polymerisations of butyl methacrylate in the presence of either linear or highly branched poly(acrylamidomethylpropane sulphonate)s (PAMPS) with dithioate end groups: using a “shell-first” approach. In a second system we produced core-shell particles with phosphate shells. Release of VEGF was shown to be controlled
by the structure and swelling of the shell. Another approach is to produce devices that can bind endogenous heparin this we have achieved by preparing hydrogels that are functionalised with triargine peptides; arg-arg-arg is a simplified model of the heparin binding domains of growth factors. Figure 1 shows the release of vascular endothelial growth factor (VEGF) and platelet derived growth factor (PDGF) is controlled by the architecture of PAMPS-based shells.

COLL 396

Polysaccharide-based core-crosslinked nanocarriers: Self-assembly assisted synthesis and biomedical applications

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In this study, various of polysaccharide-based nanogels were synthesized facilely from several polysaccharides and different monomers by using a self-assembly assisted approach. Cytotoxicity study confirmed the low cytotoxicity of these nanogels to various of cells, which indicated their promising applications in cell imaging and drug delivery. Our study disclosed potential applications of the nanogels in these biomedical fields. For example, in order to utilize these nanogels in cell imaging, several kinds of fluorescence dyes were conjugated to one typical polysaccharide-based nanogel, dextran-based nanogel, to produce fluorescent nanogels. Through adjusting the ratio of reactants, the fluorescent nanogels with various sizes ranged from 60 to 500 nm were
fabricated. Furthermore, surface modification of the nanogels were realized to prepare polysaccharide-based fluorescent nanogels with different surface charges. NGFs with various sizes and different surface charges were then co-incubated with phagocytic cells and non-phagocytic cells. Our study confirmed the feasibility of the fluorescent nanogels working as cell imaging probes. In addition, the size and surface charge of nanogels affected greatly the labeling efficiency. Besides working as cell imaging nanoprobe, the polysaccharide-based nanogels were confirmed excellent carriers for anti-cancer drug. A typical example is the successful conjugation of Doxorubicin (DOX) to dextran-based nanogels through pH-labile hydrazone bond. After capping Folic acid (FA) onto the DOX carried nanogels, the resultant composite nanogels exhibited capability of delivering DOX into the nucleus of HeLa cells.

Figure 1. Synthesis, modification and applications of polysaccharide-based nanogels

**COLL 397**

**Novel multifunctional polymer nanoparticles for active targeting in drug delivery: Application to cancer and Alzheimer's disease**

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Biodegradable polymer nanoparticles (NPs) hold great promise as they have demonstrated significant results in multiple pathologies. However, their precise functionalization in order to confer them with fluorescence (for tracing purposes) and targeting abilities is still a challenge.

Herein is reported the design of two different classes of multifunctional (*i.e.*, PEGylated, fluorescent and targeted) nanoparticles based on either poly(alkyl cyanoacrylate) (PACA) or poly(lactic acid) (PLA), two major biodegradable polymers, and their successful *in vitro* application to two major pathologies: Cancer and Alzheimer's disease (AD).
The functionalization strategy relied on the robust 'click' coupling between the polymer scaffold and the ligand of interest. For Cancer, we used biotin, folic acid or anisamide as ligands and regarding AD, we functionalized the NPs with either a curcumin derivative or a novel antibody in order to bind the β-amyloid peptide 1-42 (Aβ₁₋₄₂), a major biomarker of AD.

The synthetic pathway is thus very versatile and can be applied to a broad range of pathologies, simply by adjusting the surface decoration of the nanocarriers.

COLL 398

Antibiotic-functionalized single-walled carbon nanotubes: A means of overcoming antibiotic resistance

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As bacteria increasingly develop resistance to antibiotics, new approaches to overcoming drug resistance are needed. We report here the noncovalent functionalization of tetracycline to PEGylated single-walled carbon nanotubes (SWCNTs). The tetracycline-functionalized SWCNTs are effective against the non-resistant Dh5α strain of Escherichia coli, indicating an ability to successfully deliver this antibiotic. Tetracycline-resistant E. coli were produced by introducing the pBR322 plasmid, which codes for production of an efflux pump protein. Although the resulting E. coli...
coli were resistant to tetracycline, they were sensitive to the tetracycline-functionalized SWCNTs. These results suggest a means of using nanomedicine to overcome some types of antibiotic resistance in bacteria.

Selective amplification and a highly efficient nanoparticle-mediated delivery of DNA-cleaving agents

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Anti-cancer therapeutic agents exert their effect by causing DNA damage and subsequent induction of apoptosis. Copper-complexes are known to irreversibly modify nucleic acids and have received considerable attention because of their potential applications as chemotherapeutic agents. However, their selective and safer delivery is still a challenge. Nanoparticle mediated delivery of therapeutics has blossomed in recent years, and the potential applications are far reaching. Herein we describe a novel therapeutic strategy for delivering effective doses of DNA-cleaving agents by a defined self-assembled polymeric nanoarchitecture,

To achieve this goal, a novel copper phenanthroline (Cu-Phen-NH₂) complex was synthesized. X-ray analyses of single crystals showed that the cupric complexes of two phenanthroline molecules were able to adopt dimeric helical geometries with L2Cu2 stoichiometries in the solid state. For drug loading, both covalent and non-covalent (entrapment) strategies were adopted. Our non-covalent approach followed a co-self-assembly of amphiphilic PS-²-PAA and polyethylene glycol cetyl ether in presence of Cu-Phen-NH₂. Solvent evaporation method was used to generate particles with and without the Cu-Phen-NH₂ while covalent conjugation as was performed by carbodiimide mediated coupling. The hydrodynamic diameter of these particles was significantly different from blank nanoparticles. The in vitro properties of nanoparticles conjugated to or co-assembled with this novel ternary copper(II) phenanthroline complex (Cu-Phen) were investigated, and their ability to bind and cleave DNA under protic conditions was determined. UV-Vis spectroscopic studies revealed the binding capability of Cu-Phen with the DNA. DNA cleavage studies indicated that Cu-Phen was able to effectively cleave plasmid pBR322 DNA in the presence of H₂O₂ and ascorbic acid, as evident from gel electrophoresis assay. In vitro studies further confirmed an efficient nano-delivery of Cu-Phen complexes and indicated their capability to mediate oxidative damage to nucleobases and/or to the 2-deoxyribose moiety. Detailed physicochemical characterization and their biological studies will be presented in this talk.
Formulation and evaluation of RamaNiosomes for multiplex detection of early breast cancer biomarkers

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Early detection for breast cancer is vital to improving patient outcomes. The current gold standard is to employ mammography, however, its inherent limitations in sensitivity and specificity have garnered huge interest in developing new molecular based detection methods for absolute quantification of key biomarker expression at low levels. Furthermore, mammograms yield a high false-positive rate and expose patients to harmful radiation. To overcome these major drawbacks, Raman spectroscopy delivers real time, non-invasive, and high resolution imaging for diagnostics. Raman nanoprobe are developed for enhanced signal and multiplex detection. Here, we report the synthesis of novel RamaNiosomes consisting of deuterated lipids (15.7 ± 3.7 nm) and Raman reporter organic molecules by thin film hydration and sonication to produce diagnostic Raman imaging probes with multiplexing and ultrasensitive capability. We will discuss the physico-chemical characterization of these diagnostic probes using dynamic light scattering, zeta potential, Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy, Transmission Electron Microscopy, Nuclear Magnetic Resonance, and Raman Spectroscopy. RamaNiosomes were incubated with the breast cancer model, MCF10 cell series (MCF10A, MCF10AT1, MCF10DCIS.com and MCF10CA1a), to aid in staging breast cancer by targeting key biomarkers associated with the cancer initiation, development and progression. Cytotoxicity studies were performed using XTT method. Raman maps of cellular uptake and labelling were studied using Confocal Raman Imaging System and differential expression of biomarkers was cross validated with reverse transcription polymerase chain reaction (RT-PCR) and western blotting. RamaNiosomes have significant promise in enabling clinically relevant visualization of breast cancer progression, clinical scalability with batch-to-batch reproducibility, and may be used for delivery of therapeutics. We envision that this work will globally enable earlier breast cancer detection, treatment plans tailored to the individual and reduced the time and cost on patients.

COLL 401

Modulation of self-assembling of pyridinium cationic amphiphiles for enhanced gene delivery

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Efficient gene delivery requires controlled packing and unpacking of nucleic acids into nucleic acid-amphiphile complexes of optimum structure and physicochemical parameters. A key factor governing these two antagonistic processes is constituted by the structural and physicochemical properties of supramolecular assemblies of cationic amphiphiles, which in turn can be modulated by the structure of individual amphiphiles used in the compaction process. The recent achievements of our team towards controlling the self-assembling of various classes of pyridinium amphiphiles for enhanced gene delivery of nucleic acids will be presented, with an emphasis on interfacial engineering of these synthetic amphiphiles and comprehensive structure-property and structure-activity relationships. The interaction of amphiphile assemblies with cellular membranes and the mechanisms of internalization accessed by various classes of pyridinium amphiphiles will also be discussed.

COLL 402

A pinch of salt is all it takes: Chemistry at the frozen water surface

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Chemical interactions at the air-ice interface are of great importance to the local atmospheric chemistry but also to the concentrations of pollutants deposited onto natural snow and ice. However, the study of such processes has been hampered by the lack of general, surface-specific probes. Even seemingly basic chemical questions, such as the local concentration of chemical compounds, or the pH at the interface, have required the application of assumptions about solute distributions in frozen media. We have used glancing-angle laser spectroscopy to interrogate the air-ice interface. This has yielded several insights into the chemical interactions there. The environment at the interface between air and freshwater ice surfaces is distinct from that at the interface between air and liquid water. Acids such as HCl that adsorb to ice surfaces from the gas phase result in significantly different pH responses than at liquid water surfaces. Further, the solvation of aromatic species is suppressed at freshwater ice surfaces compared to at liquid water surfaces, leading to extensive self-association of aromatics at ice surfaces. Photolysis kinetics of these species are much faster than at liquid water surfaces; this can sometimes (but not always) be explained by red-shifts in the absorption spectra of self-associated aromatics increasing the extent to which solar radiation is absorbed. By contrast, the extent of hydrogen bonding and the solvation of adsorbed species are similar at liquid water surfaces and at frozen saltwater surfaces. Adsorbed acids and bases evoke similar pH responses at frozen saltwater ice surfaces and liquid water surfaces, and photochemical kinetics of at least some aromatic compounds at frozen saltwater ice surfaces are well-described by kinetics in liquid water.
COLL 403

Natural organic matter as an important photosensitizer in snow and ice

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It is well established that ice is a reactive medium in the environment and that active photochemistry occurs in frozen systems. Snow and ice contain a number of absorbing species including nitrate, nitrite, peroxide, and organic matter. These generate a variety of reactive intermediates upon radiation, such as hydroxyl radical and singlet oxygen. Dissolved organic matter (DOM) is a ubiquitous component of snow and ice and plays an important role in overall light absorption properties of the sample. Additionally, the reactive intermediates produced by DOM photolysis can further react with contaminants present and alter their fate in the environment or may play a role in generation and emission of volatile species to the overlying atmosphere. Unfortunately, the role of DOM in ice photochemistry has received little attention, and characterizing the nature of DOM is hindered due to its complex and heterogeneous nature. Using ices generated under controlled laboratory conditions we have found that the production of reactive oxygen species from DOM photolysis is enhanced in ice compared to liquid water, and this production significantly influences the fate of organic contaminants in ice. We will also discuss here advances in the characterization of DOM using advanced analytical techniques such as ultra-high resolution mass spectrometry and NMR.

COLL 404

Cryo-transmission electron microscopy for the analysis of marine vesicles in the bulk, sea surface microlayer, and aerosol phase

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Membrane vesicles in the marine environment are thought to act as high local concentration reactors for organic material in the ocean, and their ejection into the atmosphere as aerosol particles has been proposed as an important step evolution from prebiotic life. Chisholm et al. recently made the first observation of these vesicles and showed through dry state transmission electron microscopy (TEM) that membrane vesicles make up a small but significant proportion of the sub 200 nm colloidal particles observed in sea water. However, cryo-transmission electron microscopy is the most adept tool for imaging colloids in solution, allowing their structure to be trapped in its natural environment. Applying this techniques to the study of bulk sea water, the sea surface microlayer (SSML) and aerosols using a marine aerosol reference tank (MART) we have been able to show a concentration of structurally complex membrane vesicles in the SSML and investigate their transfer to the aerosol phase. The ability to image
ocean colloids in their natural state promises to afford great insight into the transfer of chemical information in the marine environment.

**COLL 405**

**Effects of organic matter on pollutant photolysis at ice surfaces**

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Ice presents an important reaction environment for many atmospheric compounds including pollutants such as polycyclic aromatic hydrocarbons (PAHs). Photochemistry of PAHs has been shown to proceed much more quickly at ice surfaces than in bulk ice or in liquid water. Common components of natural waters such as salt and organic matter could affect pollutant reactivity at ice surfaces, but few studies have investigated this possibility. We have measured PAH photolysis kinetics in aqueous solution, in bulk ice, and at ice surfaces in the presence of proxies for environmental organic matter. Our results show that organic matter can significantly affect PAH photolysis kinetics in bulk ice and at ice surfaces, even when the organic matter does not absorb sunlight.

**COLL 406**

**Photochemistry at ice interfaces**

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Photochemical reactions of impurities in natural snow and ice are important because they: (1) release reactive gases – such as nitrogen oxides (NO$_x$) and molecular halogens – to the atmosphere, (2) transform pollutants in snow and ice, and (3) alter the composition of the snow/ice, which can influence ice core records of past atmospheres. Understanding these impacts requires quantifying the photochemical kinetics of solutes, which is complicated by the fact that they can be present in different reservoirs in/on the ice. These include at the air-ice interface, at the interface between ice grains, and within the bulk ice matrix. Past work suggests that reactions at the air-ice interface can be enhanced relative to reactions in the other reservoirs, but this is an unresolved issue. To examine this question, we are using two complementary approaches. In the first, we are employing 3-D X-ray computed tomography to image the locations of solutes in laboratory ice samples frozen using different techniques. For the second approach, we are characterizing the photochemistry of solutes in ice samples prepared with these different freezing techniques to see how photon fluxes and photochemical kinetics vary between the three ice reservoirs.

**COLL 407**

**Spectromicroscopic observation of sea spray composition and aging**
The ability to perform spatially resolved spectroscopy at the nanoscale is crucial for studying individual nanometer sized sea spray particles. Specifically, scanning transmission X-ray microscopy coupled with near edge X-ray absorption fine structure (STXM/NEXAFS) spectroscopy is used to determine elementally specific molecular information on organic and inorganic species with a 30 nm spatial resolution. To date, particles collected in many laboratory and field studies have been analyzed using STXM/NEXAFS to study their composition as it relates to their cloud forming properties. Not only does secondary organic aerosol formation change the composition of the particles, but also the biological activity of the ocean plays an important role in determining the organic fraction of the particles. We have created a method to estimate mass fractions for implementation in hygroscopicity parameterizations used in cloud models. Aerosol hygroscopicity is sensitive to organic material, so measurements such as this can add physical insight into changes in CCN for complex samples containing externally/externally mixed particle populations. This talk highlights the importance of characterizing the single particle composition for laboratory and field collected particles in order to gain insight to their physical properties in the atmosphere.

COLL 408

Composition of the sea-salt solution-air interface as affected by organics

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The aim of the experiments was to obtain surface composition of mixed halogenide / organic acid solutions of relevance to the atmospheric chemistry in marine environments with X-ray photoelectron spectroscopy (XPS) on a liquid microjet. The surface composition of sea spray particles is crucial in the chemistry with gas phase oxidants. Organics present at these interfaces derive from surface active degradation products from marine biota accumulating at the ocean surface.
Previous XPS studies showed that halide ion concentrations are enhanced at the aqueous solution air interface. A first XPS study KI solutions with butanol indicated the importance of specific interactions of the cation with the alcohol headgroup. Here, we looked into the effect of butanoic acid and of a more complex organic compound, citric acid, on the presence of Na⁺ and halide ions at the interface. Measurements were made at the SIM beam line of the Swiss Light Source at the Paul Scherrer Institute.

The results show changes in Br 3d and Na 2s PE signals with increasing citric acid concentration. In the case of 0.12M NaBr in the presence of 2.5M citric acid, 40% ± 10 more Na⁺ ions are present within the probe depth of the experiment than in neat NaBr solution. On the other hand, Br 3d signal are suppressed from the interface. We performed parallel experiments with similar solutions in a flow tube related to the kinetics of bromide with ozone. In presence of the organic, the uptake coefficient of ozone did not depend on the gas phase ozone concentration as observed in a recent study in absence of organics. That behavior was attributed to a surface process on neat halide solutions. Careful analysis of the kinetics is needed to assess the relative contribution of surface and bulk processes in presence of organics.

COLL 409

**Challenges in replicating the surface of sea spray aerosols in laboratory investigations**

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Sea spray aerosol particles play an important role in controlling the composition of the atmosphere by acting as surfaces upon which heterogeneous reactions occur. Recent studies have shown that sea spray, particularly at the surface, is highly complex and thus to understand the composition of the atmosphere in marine environments, laboratory experiments must move beyond using simplistic model systems. In order to increase the complexity, many methods have been used for generating sea spray in the lab. The most common methods create bubbles in natural seawater using a variety of approaches, ranging from sintered glass frits to impinging water jets on the seawater surface. The composition of sea spray is highly sensitive to the production method and thus in order to fully understand the reactivity of atmospheric aerosols, one much use production methods that accurately mimic breaking waves. As part of studies in the Center for Aerosol Impacts on Climate and the Environment (CAICE), we have developed a new laboratory method for replicating sea spray in the laboratory. In this presentation, an overview will be provided, describing how the complexity of the ocean-atmosphere system was transferred into a laboratory setting to characterize the chemical complexity, heterogeneous reactivity, and climate properties of sea spray. Breaking waves in natural seawater pumped directly from the ocean are used to produce sea spray particles which are sampled into an array of state-of-the-art instruments for analysis. Results from experiments will be described demonstrating how
changes in seawater composition due to biological processing affect the chemical complexity of sea spray.

**COLL 410**

**Stimuli-responsive cellulose nanocrystals and their composites**

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Cellulose nanocrystals (CNCs) have attracted attention in recent years as potential green reinforcing fillers for polymer nanocomposites. A key aspect of these materials are the interactions between the CNC and matrix polymer and as well as between the CNCs themselves. We have recently shown that sulfonated CNCs (from a range of different biosources such as tunicates, cotton and microcrystalline cellulose) embedded within a variety of polymer matrices (including poly(vinyl acetate), poly(ethylene oxide-co-epichlorohydrin), polybutadiene and polyurethane) show mechanical switching upon exposure to water. It is proposed that in the dry state hydrogen bonding interactions between adjacent CNCs play a role in this reinforcing network, transferring mechanical stresses across the sample, and resulting in stiff materials. Once the water diffuses into the nanocomposite, it competitively hydrogen bonds to the CNC surfaces disrupting the stress-bearing CNC percolating scaffold and softening the nanocomposite. More recently, we have shown that we can control the aggregation of the CNCs by altering their surface chemistry. For example, putting carboxylic acid or amines moieties on the CNC surface yields pH-sensitive dispersions that at an appropriate pH form gels. Incorporation of these pH-sensitive CNCs into a polymer matrix yields pH-responsive nanocomposites. This presentation will focus on our latest results on functionalization of the CNCs to control their aggregation/dispersion as well as studies on the properties of their corresponding nanocomposites.

**COLL 411**

**Graphenes and their self-organization**

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Graphene-type molecules, typically large polycyclic aromatic hydrocarbons (PAHs), have gained enormous interest because of their unique self-organization behavior and promising electronic properties for applications in organic electronics. The attachment of alkyl side chains leads to the formation of a well-defined supramolecular columnar organization, while the local separation between the flexible alkyl fraction and the rigid aromatic part induces discotic liquid crystalline phases. The transition temperatures between different phases strongly depend on the geometry of the substituents and the size and geometry of the aromatic core. An additional powerful tool are supplementary non-covalent interactions including hydrogen bonding, dipole-dipole and ionic forces
which are incorporated within the core periphery to further control and improve the molecular packing within the columnar stacks. This chemical approach allows to tune precisely the local charge carrier transport within the one-dimensional pathways. From the processing side, the disc-shaped graphenes can be arranged in two ways on the surfaces for different device configurations: face-on and edge-on. The face-on can further induce a homeotropic orientation of the columns perpendicular to the surface which is considered to enhance the solar cell efficiency. On the other hand, the edge-on arrangement leads to the growth the stacks parallel to the surface which is required in field-effect transistors. An improvement of the charge carrier transport in transistors can be reached by an uniaxial orientation of the columnar structures between the source and the drain electrode, since structural defects as trapping sites are avoided.


COLL 412

Supernanoparticle synthesis based on PEI-Au clusters

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The field of plasmonics fuels the formation of nanoparticle aggregates which feature novel optical and plasmonic properties. One strategy is to increase the complexity by the controlled formation of nanoparticle aggregates. In such configurations, the plasmonic coupling of the individual particles can exhibit novel properties.

While a lot of research is devoted on the theoretical understanding of such nanoparticle aggregates, synthetic routes to form these materials are still relatively scarce.[1] Here, a conceivable approach is introduced, which permits the formation of PEI-Au nanoparticle superaggregates.[2] The amine functions of the PEI can bind the gold salt which is reduced at elevated temperatures to form small gold nanoparticles. During the reaction the initially soluble polymer undergoes cross-linking reactions and a stable polymer shell is formed, which encapsulates a large number of individual Au nanoparticles. The size of the superaggregates can be tuned by the control of the ratio between the PEI and the Au nanoparticles.

One important parameter for the utilization of such supernanoparticle aggregates for plasmonic applications is the achievable filling factor. Different synthetic strategies to tune this filling factor include seeded-growth approaches to enlarge the nanoparticle size within the superaggregates. UV-vis spectra obtained from individual nanoparticle
aggregates by darkfield microscopy are in good agreement with theoretical predictions of the optical properties of the aggregates.

Next to the optical characterization different strategies to self-assemble these superparticles into ordered patterns are introduced with the aim to further tune the optical and plasmonics properties of the structures.


DOI: 10.1002/ppsc.201300309


COLL 413

Supramolecular solvent-free nanofluids: Reagents, coatings, and new physics

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We show that auto-condensation of organoalkoxysilanes, followed by suitable anion exchange, produces solvent-free nanoparticle nanofluids we call organosiloxane supramolecular liquids. We find that classical liquid properties are exhibited with some
distinct differences. We observe heat capacity anomalies manifested as lambda transitions in excess heat capacity centered around a glass transition ($T_g$) and around a freezing transition. The $T_g$-proximal lambda transition is the first experimental realization of an enthalpic phase transition overlying a glass transition. The existence of such a connection or coincidence has undergone decades of theoretical conjecture. The second anomaly spanning the melting/freezing range is the first reported excess enthalpy ever reported for an experimental particulate fluid undergoing a phase transition. The integral enthalpy from these lambda transitions is quantitatively accounted for by the loss of specific surface area of the particles, and the associated surface free energy, upon freezing and upon cooling beneath the glass transition temperature. This new material and cousins to be similarly derived promise to become useful in developing soft-sphere potentials in the thermodynamics of polymeric liquids. Similarly composed nanofluids obtained by condensation on nanosilica core templates and surface decorated with both ionic liquid organic salt groups and with various reactive groups are exotic cross-linking agents that define new types of resins and reagents. Such agents can be used to counter embrittlement provided by nanofillers while increasing toughness. We show that such materials can be used to produce thin films including UV protective clearcoats and an interesting new family of adhesives.

**COLL 414**

**Engineered conjugated polymer nanoparticles for glycosaminoglycan profiling in a urine simulant**

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Conjugated polymer nanoparticles (CPNs) are soft nanoparticles fabricated by self-assembly of non-aqueous soluble aromatic p-electron conjugated polymers (CPs) in aqueous solutions. CPNs exhibit excellent luminescent and biophysical properties, suitable for biological applications including labeling, delivery, and monitoring of biological substances. We have previously reported that physically and photophysically stable CPNs were formed by treating primary amine-containing CPs with organic acids followed by dialysis, and the resulting cationic CPNs can further undergo structural reorganization to maximize interpolymer hydrophobic interaction when treated with an carboxylated anionic polysaccharide, hyaluronic acid. From the observation, we hypothesized that polysaccharides with different ionic strengths (i.e., sulfated heparin etc.) can modulate the aggregation properties of CPNs through the ionic interaction between CPs and polysaccharides, resulting in photophysical property changes of CPNs by the reorganization of CP chains. In this presentation, design/fabrication of CPNs with different backbone structures and a multiarray sensor to differentiate structurally similar anionic polysaccharides, glycosaminoglycans (GAGs), in a urine simulant will be discussed.
COLL 415

Self-assembly of colloidal molecules

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Introducing specific directional interactions between colloids has the potential to assemble colloids in a programmable fashion into 3D architectures for applications in photonic, plasmonics, or catalysis. The presentation will introduce multiple synthetic methodologies for the formation of either colloidal patchy particles for directional self-assembly via noncovalent interactions or colloidal particles with well-defined multicavities that can be assembled using depletion forces. The assembly of these colloids into colloidal molecules and larger aggregates will be discussed.

COLL 416

New approach to polymeric organic nanoparticles useful for biology and medicine

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Metal nanoparticles (NPs) have been studied intensively because of their potential applications in biomedicine, catalysis, and optical and electronic fields. Their most serious limitations are related to potential toxicity and the difficulty in producing NPs with a single reactive surface group. This talk will describe a new approach to organic nanoparticles (ONPs) that are monovalent, biocompatible, and capable of carrying multiple fluorophores or other units. The application of these ONPs as improved fluorescent probes for chemical biology and their potential application as drugs and as drug and cell delivery agents will be discussed.
Supra-amphiphiles: A new bridge between colloids science and supramolecular chemistry

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Besides the conventional amphiphiles, there is an emerging research area of supra-amphiphiles, which are constructed on the basis of noncovalent interactions and dynamic covalent bonds. In this presentation, we will give a general introduction on the concept, design principles and topologies of supra-amphiphiles, starting from some rational-tailored building blocks. In addition, we highlight some progress on the combination of molecular architecture and functional assembly of supra-amphiphiles. For example, we will discuss how to employ the concept of supra-amphiphiles for fabricating light-emitting organic materials and fluorescent-based chemical sensors. Moreover, we will introduce how to fabricate porphyrin based supra-amphiphiles for enhancing the effective energy transfer from light to triplet oxygen, leading to improvement of the efficiency of photodynamic therapy in mild conditions. To summarize, the supra-amphiphile is a new bridge between colloids science and supramolecular chemistry, and it is a field where we can make full use of our imaginative power.

Surface chemistry at dual-perimeter sites on the Au/TiO₂ catalytic surface: Unzipping the alkyl groups in adsorbed carboxylic acids a step at a time

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The catalytic activity of the perimeter sites at the nanoparticle Au/TiO₂ interface was observed by IR spectroscopy in the oxidation of CO at low temperatures, where CO adsorbed on the TiO₂ support surface was selectively oxidized compared to CO adsorbed on Au. It is found that the O₂ molecule is dissociatively activated by chemisorption at the dual Ti⁴⁺Au sites at the Au perimeter, with an activation energy of 0.5 eV. We have extended this idea to the oxidation of acetic, propionic and butyric acids, where stepwise oxidative attack of the alkyl group can be monitored. For the two higher acids, under oxidation conditions, sequential dehydrogenation steps to produce a C=C bond first occurs at the C₂-C₃ molecular site, followed by C-C and C-O bond scission to yield the rather exotic Au₂=C=C=O (gold ketenylidene) species on the way to CO₂ formation. Acetic acid also produces Au₂=C=C=O species. The results indicate that high selectivity in the oxidation of carboxylic acids occurs at these Au/TiO₂ catalytic sites.

**COLL 419**

**Comparative study of organothiol adsorptions, desorptions, and reactions on gold and silver nanoparticles in water**

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Self-assemblies of organothiols (OT) and thiolated biomolecules onto gold and silver have remained as one of the most active research areas in nanoscience and molecular interfacial phenomena. One common belief is that organothiol forms monolayer adsorption onto gold and silver surfaces, and the structure and properties of the organothiols on gold and silver are similar. However, recent researches conducted in our lab with a series of aromatic and alkyl thiols reveals that OT adsorption, desorption, and reactions on gold nanoparticle (AuNPs) in water can be significantly different from that on silver nanoparticles (AgNPs) in water. OTs form monolayer adsorption onto AuNPs by releasing the sulfur-bound hydrogen as a proton and acidifying the ligand binding solution, but the aromatic OTs continuously reacts with AgNPs until total consumption of AgNP or OTs occurs. These reactions convert AgNPs into insoluble RS-Ag complexes, inducing no detectable pH change in the OT/AgNP solutions. On the other hand, long-chain alkanethiols adopt monolayer adsorption on both AuNPs and AgNPs, and the alkanethiols are drastically better ordered on AgNPs than on AuNPs. Sodium borohydride induces organothiol desorption or desulfurization from both AuNPs and AgNPs. However, the OT desorption and desulfurization efficiencies on AgNPs are significantly lower than that on AuNPs, and the effect of the sodium borohydride on the morphology for the as-synthesized colloidal AgNPs are markedly different for AuNPs. In addition to providing a side-by-side comparison of the OT adsorption, desorption, and reaction on AuNPs versus on AgNPs, a unifying mechanism will be discussed in this presentation for those stark differences in the structure and properties between OT on AuNPs and AgNPs.
Properties of nanosized islands and their influence on unimolecular reactions

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Scanning tunneling microscopes (STMs) open the fascinating possibility to investigate the specific properties of material on the nanoscale. The physics of nanostructures and the chemistry of single molecules are accessible. We employ this technique in order to understand the properties of nanostructures and their influence on the diffusion and reaction of molecules. In particular, our latest results on the confinements of the interface state in nanosized islands of NaCl on Ag(111) will be presented first. On this hybrid system, we investigated the diffusion of water molecules. Finally, a bistable dye molecule was adsorbed on the system and investigated with respect to its usability as a molecular switch. The results of diffusion and isomerisation are compared to studies on the pristine metal samples.

Figure: False-color 3D view of Hybrid surface with 4,4'-di-hydroxy-azobenzene molecules adsorbed before and after exposure to light.

Coll 421

Interfacial charge transfer and reactivity of supported metal oxide nanoclusters
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The unique catalytic activity of supported nanoparticles versus their bulk counterparts is often attributed to electronic interactions with the support that result in charge transfer, structural changes or creation of new active sites at the particle-support interface. For oxide supported Cu catalysts, which are of interest for promoting the water-gas-shift (WGS) reaction and methanol synthesis, the metal oxide-Cu electronic interactions are known to strongly influence activity. In this work, we are using size-selected deposition to explore the interfacial electronic structure of a number of small metal oxide clusters (Mo, W, Ti, Nb) on Cu(111) and Cu\textsubscript{2}O/Cu(111) surfaces as model “inverse” catalysts. Such inverse systems are useful for investigating the chemical role of the oxide, and in some cases, can be even more active than the conventional catalysts as a result of electronic modifications induced by the metal substrate, e.g., higher state of reduction. The extent and direction of charge transfer at the interface are extracted from coverage dependent work function measurements using two-photon photoemission (2PPE) and theoretical DFT calculations. The trends observed for charge transfer are correlated with their ability to dissociate adsorbed water molecules, which is an important step in the WGS reaction. As O-vacancies can play an important role for adsorbate binding and water dissociation on oxide surfaces, both stoichiometric and sub-stoichiometric oxide clusters, e.g., Nb\textsubscript{4}O\textsubscript{10} and Nb\textsubscript{4}O\textsubscript{7} clusters, are being studied. These studies highlight the unique ability of cluster deposition to prepare well-defined “reduced” surface oxides by controlling the stoichiometry of the clusters rather than by post-deposition heating or chemical treatments.

COLL 422

Reactivity of oxide and sulfide supported metal nanoparticles: Role of the interface

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While the reactivity of metallic nanoparticles, as function of shape, size, composition and support has been the subject of many investigations, more recently attention has focused on the role of interfacial and perimeter sites as they may facilitate strong mixing of the wave functions of the reactants, nanoparticle, and the substrate atoms. However subtle differences in the local electronic structure at the interface may control whether the active sites lie there or elsewhere in the system. Given the recent interest in single layer MoS\textsubscript{2} and the large number of studies already carried out on titania, we present here a comparative examination of the microscopic details of CO oxidation and methanol decomposition on sub-nanometer sized metal nanoparticles (Au, Ag, Pt), supported on single layer MoS\textsubscript{2} and on TiO\textsubscript{2}(110). Calculations of activation energy barriers, reaction pathways, and pre-exponential factors are based on density functional
theory (DFT). Reaction rates for selected cases (for which experimental data is available) are obtained from kinetic Monte Carlo simulations performed with energetics obtained from DFT. The role of charge transfer at the interface, charge redistribution on the nanoparticle and their impact on the formation and scission of specific bonds will be presented in detail. In particular, activation mechanisms which were found to be applicable for both CO oxidation and methanol decomposition at the interface of Au/TiO$_2$ [1] will be probed for the same reactions on the nanoparticle-MoS$_2$ interface to check for their generality.


Work supported in part by DOE grant DE-FG02-07ER15842.

COLL 423

Contact electrification between liquids and polymers: Possible route for mechanochemical synthesis

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The accumulation of electrostatic charge on materials via contact electrification (tribocharging) is ubiquitous but the molecular processes by which it occurs are still not fully understood. This talk will show that the charging of liquids flowing through capillaries is consistent with the triboelectric series for solid materials. Calculated values of $\Delta G$ and $\Delta G^\ddagger$ for neutral, charged, and radical species 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, and to determine whether the predicted intermediates can be harnessed to perform mechanochemical synthesis.

COLL 424

Implications of uncertainty on computationally predicted rates and trends in catalytic ammonia synthesis

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Using a general method for estimating the exchange-correlation uncertainty in density functional theory calculations we estimate the uncertainty on catalytic rate of ammonia synthesis over a range of transition metal catalysts. In general the estimated error is
significantly reduced due to correlations in the error between various intermediates and surfaces, highlighting the need for systematic methods of error estimation. Uncertainties are shown to be a complex function of reaction condition and catalyst material, and we demonstrate that relative rates between different catalysts are better described than the absolute rates. A new approach is introduced where catalysts can be screened based on the probability that their rate will be an improvement over a given standard, rather than on the basis of absolute predicted rates. The implications and challenges of analyzing sources of uncertainty beyond exchange-correlation energy are discussed, along with the potential opportunities for application of the probabilistic approach to other areas of computational materials design.

COLL 425

Amphiphilic macromolecules as cardiovascular therapeutics: Probing interactions with scavenger receptors

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Atherosclerosis, the primary pathology underlying cardiovascular disease, is an inflammatory disease characterized by the accumulation of oxidized low-density lipoprotein (oxLDL) in the vascular intima, its uptake by macrophages, and the subsequent formation of foam cells and arterial plaque. Nanoscale amphiphilic macromolecules (AMs) comprised of a sugar backbone, branched aliphatic chains, and a hydrophilic poly(ethylene glycol) (PEG) tail have shown promise as atherosclerosis therapeutics through inhibiting scavenger receptor-mediated oxLDL uptake in macrophages. Previous research indicated that AMs' hydrophobic domain modulates their bioactivity, possibly through hydrophobic interactions with scavenger receptor binding domains. As certain scavenger receptors present amines within their binding pockets, we hypothesized that incorporating heteroatoms into AMs' hydrophobic portion would provide enhanced physical interactions between AMs and scavenger receptors through hydrogen bonding, thus increasing AM bioactivity. To this end, a series of AMs comprised of tartaric acid backbones, methoxy-terminated aliphatic chains of varying hydrophobicity, and different molecular weight PEG tails was synthesized then compared to a series of AMs containing no methoxy moieties. AM chemical structures were confirmed by nuclear magnetic resonance spectroscopy and gel permeation chromatography. As AMs typically self-assemble into nanoscale micelles, dynamic light scattering and fluorescence spectroscopy were used to determine hydrodynamic diameters and critical micelle concentrations, respectively. Finally, AMs' cytocompatibility as well as ability to inhibit oxLDL uptake in macrophages were assessed.
Tobacco mosaic virus as polyvalent scaffold to stimulate humoral immune responses

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Viral nanoparticles can serve as powerful platforms to display multivalent functional groups for biomedical application by orthogonal bioconjugation and supramolecular strategy between host and guest molecules. Such multifunctional TMV can load with orthogonal imaging agents, targeting ligands and drugs in one-pot approach. In addition, we showed that, through chemical modification, tobacco mosaic virus (TMV) and cowpea mosaic virus (CPMV) can be employed as effective carriers to display small molecule haptens in high density and ordered pattern with improved humoral immune responses in vivo.

Exploring the molecular bases of cytoskeleton-cell membrane interactions, by live imaging approach
Cellular architecture and compartmentalisation are organised as bi-dimensional fluid membranes, which are assembled by essential molecules for the life of a cell: the phospholipids. These are crucial for the cell membranes formations and play a pivotal role, together with proteins, in the organisation of “raft” domains at the membrane level. In addition, they participate in several other fundamental cell mechanisms including proteins regulations, vesicular trafficking and cell motility. However, cell membrane dynamics still represent one of the most complex process yet to be fully elucidated. In fact, bio-molecules such as phospholipids, sphingosines and sterols cannot undergo genetic modifications and, hence, being then analysed in live cells using traditional fluorescence protein approaches.

In this work, we used polymersomes as synthetic self-assembled delivery system to achieve optimal distribution, in live cells, of five different membrane and cytoskeleton probes: BODIPY-Phosphocholine, NBD-Cholesterol, BODIPY-TR-Sphingosine, TopFluor-PI(4,5)P2 and Phalloidin-ATTO647. Using such an approach, we have been able to elucidate the cooperation between lipid (PIP2 in particular) domains and cytoskeleton during cellular mechanisms such as adhesion and spreading process, showing a peculiar active transportation to the membrane protrusion.

In conclusion, this work enables to reach a better understanding of the complexity of lipid organization, and provides important explanation about the interplay that subsists between these bio-molecules and the F-actin network in live cell.
Toolbox of differently sized and labeled PMMA nanoparticles for cell studies

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The RAFT polymerization of methyl methacrylate to poly(methyl methacrylate) (PMMA) yields well defined, biocompatible polymers that can easily be labeled with a broad variety of fluorescent dyes by postmodification of the polymer backbone or by using dye labeled monomers during polymerization. The formulation into fluorescent nanoparticles via nanoprecipitation opens a toolbox of differently sized and labeled polymeric nanoparticles with narrow size distributions that can be used for internalization and toxicity studies. The localization of the nanoparticles was detected after certain time points by confocal laser scanning microscopy and flow cytometry investigations. In the end, uptake mechanisms was studied depending on the particle size by co-localization with marker for late endosomes and lysosomes and using specific inhibitors for endosomal uptake. We show that surfactant-free particles show significant variations depending on the particle size.
Figure 1. Schematic workflow of the synthesis of labeled polymers, formulation of different sizes of labeled particles and images of the uptake studies in human cell lines.

References:


COLL 429

Investigation of nanostructured metal-organic frameworks used in cancer research

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Cancer is a complex and multifactorial disease accounting for more than ten million new cases every year. Nanotechnology platforms with high target specificity and minimum collateral damage and immune reaction are currently under development. Nanoscaled metal-organic frameworks were produced and characterized, which showed versatile vectors for theranostics applications with a significantly high cytotoxicity to Chinese hamster ovarian (CHO) cancer cells. To fully understand the therapeutic efficacy and mechanism of CHO cancer damage, we took these steps: 1) nanomaterials synthesis; 2) fine structural characterization; 3) properties measurement; and 4) the efficiency of the theranostics analysis. In-vitro toxicity data indicated that PCN-95 IC₅₀ (0.02 ppm) is comparable to, or lower than the current first-line drug formulations; at higher doses, the kinetics of action were approximately ten-fold higher. These biological effects may be attributed to the unique tetra-topic carboxylate ligand bridging to a bimeric µ₃-H₂O-centered cluster, in addition to high crystallinity and high aspect ratio.

COLL 430

1D origami arrays

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Arrayed DNA origami provide the opportunity to study assembly kinetics and yield by presenting identical species with known orientations to the solution media. One dimensional arrays can be generated via the polymerization of origami oligomers. This process can result in the formation of arrays which are too long and/or tangled to be readily characterized using standard AFM sample preparation methods. We will describe the use of of tagged chain termination species in polymerization reactions to significantly reduce the extent of polymerization, yielding finite arrays amenable to AFM characterization. This mechanism of producing finite 1D arrays will be compared with other methods of 1D array fabrication.

**COLL 431**

**Engineering stimulus-responsive nanoparticles in liquid media: Implication of ionic strength and surface chemistry on adsorption and fluid phase partitioning in aqueous/toluene and cellular systems**

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Understanding the physico-chemical properties of nanoparticles at fluid-fluid interfaces is of significant importance in diverse areas of science and technology, including water-oil separation, food processing, and biodistribution. Though recent studies offer new perspectives for the development of responsive nanomaterials that can be used to confer stability to disperse fluid/fluid systems, the mechanisms by which this occurs are only partially understood.

Here, we investigate the role of hydrophobicity on the equilibrium and transport properties of responsive nanoparticles in biphasic systems and compared oil-water partition with cellular uptake. We utilize gold nanoparticles grafted with stimulus-responsive copolymers consisting of di(ethylene glycol) methyl ether methacrylate (x = MeO₂MA) and oligo(ethylene glycol) methyl ether methacrylate (y = OEGMA), or Au@(MeO₂MAₓ-co-OEGMAᵧ) NPs. Variation of the (x:y) copolymer ratio directs lower critical solution phenomena allowing tunable hydrophobicity both by polymer composition and external stimuli such as temperature or ionic strength.

We study the implications of ionic strength and copolymer composition on the adsorption dynamics of Au@(MeO₂MAₓ-co-OEGMAᵧ) NPs at the toluene-water interface using axisymmetric drop shape analysis (ADSA) and relate the results to the adsorption constant and the fractional surface coverage, f. The increase in hydrophobicity from (x:y)=80:20 to (x:y)=95:5 is accompanied by an increase in the surface coverage from f=0.3 to f>1, or multilayer adsorption. Similarly, partition of nanoparticles between aqueous and toluene phases shows a strong function of the copolymer composition, from $K_{TW}(80:20) = 0.7$ to $K_{TW}(95:5) = 9.8$. 
By comparing the toluene-water distribution of NPs with cellular uptake we demonstrate that the partition coefficient in a model oil/water system plays a significant role in intercellular transport processes. Specific knowledge of $K_{T/W}(y, I)$ enables design of fluid/fluid stability as a function of the copolymer ratio and stimulus fields, and can be a predictive metrics for cellular uptake of NPs with variable surface chemistry.

**COLL 432**

**Point-of-care diabetes monitoring via breath acetone detection**

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Diabetes can be a life-long disease which requires continuous blood-glucose monitoring. Currently technology, albeit good, does have its draw-backs; in particular that it is an invasive technique which causes discomfort to the individual. Therefore, low compliance can ultimately lead to other health issues. Approaches are underway to develop a portable, hand-held, noninvasive monitoring device to detect the biomarker, acetone, found in the breath of diabetics. By creating films of poly(4-vinylbenzenesboronic acid) and poly(allylamine hydrochloride), acetone can react with these via a Petasis reaction. This alters the physicochemical nature of the film, providing a quantification of acetone, and thus hopefully blood-glucose levels, in a non-invasive manner.

UV-transmitting poly(methyl methacrylate) slides are coated with a system of PAH/PVBBA at differing pH values and are then exposed to acetone/water vapor. The slides are next subjected to the light emitted by a diode with a peak wavelength of 300 ± 5 nm. The transmitted light is detected by a UV-photosensor with an integrated transimpedance amplifier that produces a voltage output as a function of absorption.

We have been able to develop a technology that accurately detects acetone vapor. We are engineering a hand-held breathalyzer device to detect acetone in the breath of diabetic individuals and are attempting to optimize its capabilities.

**COLL 433**

**3D multiresolution microscopy for the visualization of the transient interactions of viral-scale particles with live cells**

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Cellular uptake of extracellular material is a vital function which allows cells to sample and respond to their environment. Nanoscale objects, such as viruses, are able to utilize
this critical function to invade and infect cells. The entire viral infection process covers multiple spatiotemporal scales, from the nanometer-scale size and microsecond diffusive behavior of extracellular virus particles to the 10s of micron and minute to hour scale over which the cells respond to this viral attack. This type of multi-scale phenomena is impossible to follow with existing imaging techniques due to the combination of high speed dynamics and both small and large scale motions in three dimensions. To provide unprecedented insight into this multi-scale process, we have developed a 3D multi-resolution microscope, capable of extracting the dynamics local to a viral-scale particle with high spatiotemporal precision (down to 10 nm and 10 µsec in all three dimensions) while simultaneously mapping the micron scale 3D cellular contour.¹ This 3D multi-resolution microscope was applied to the early stages of cellular uptake of viral scale nanoparticles labeled with semiconductor quantum dots and the Tat peptide derived from HIV-1. We demonstrated, for the first time, full 3D visualization of the landing of a freely diffusing viral-scale particle on the 3D cellular contour, allowing us to extract the long range interaction dynamics between the cell membrane and the invading nanoparticle. After a landing event, the nanoparticle's search of the complex 3D membrane terrain uncovered an unexpected correlation between sub-diffraction membrane structure and local particle dynamics. This new method promises to unveil critical interaction dynamics in the viral infection process, which will ultimately lead to new insights in both antivirals and therapeutic cellular delivery strategies.


COLL 434

Interactive displacement reactions in the surface oxidation chemistry of metallic gold

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Metallic gold is unusually selective for oxygen-assisted coupling reactions. In these processes, both on model single crystal systems and under catalytic reaction conditions, competitive displacement reactions dictate the optimum reaction conditions for maximum product selectivity. A general study of these reactions will be presented, including both theory and experiment. The inclusion of weak van der Waals interactions for properly scaling the stabilities of reaction intermediates is of significant importance.

COLL 435

Surface chemistry of hydrocarbons

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X-ray photoelectron spectroscopy (XPS or ESCA) is a versatile tool to investigate chemical reactions on surfaces. At third generation synchrotron radiation facilities, such as BESSY II in Berlin, XPS studies can be performed with high resolution and in situ, during adsorption or during heating. From the binding energies of the adsorbate and substrate core levels, detailed information not only on the chemical composition, chemical state and adsorption sites, but also on the vibronic final state in the photoemission process itself can be derived. In this presentation, three different examples concerning the adsorption of hydrocarbons will be addressed [1]. The first deals with the adsorption of small saturated and unsaturated hydrocarbons on metal surfaces. From high-resolution XP spectra, detailed information on adsorption sites, dissociation and the formation of new species are derived. The second example addresses the formation of supported graphene on metal surfaces, including the introduction of hetero-atoms such as nitrogen and boron in the lattice. Finally, the third example concerns the adsorption and reaction of a much more complex molecule, namely the liquid organic hydrogen carrier (LOHC) dodecahydro-N-ethylcarbazole, on metal surfaces. Hydrogen storage in LOHCs is a possible future technology to circumvent the challenges in hydrogen storage.


COLL 436

Towards screening models for metal/oxide pairings in catalysis

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Oxide supported metal nanoparticles are the mainstay of the chemical catalysis community. From subnanomaters to several nanomaters the metal particle can be in its reduced form, oxidised or subject to the strong metal support interaction. Transition metal and rare earth oxides are still difficult for standard DFT methods to simulate, obtaining band-gaps that are too small -sometimes no band gap in the case of PdO. This talk will take three metal oxides La2O3, PdO and CeO2 to discuss some of the short comings and how we have been using DFT+U as a pragmatic tool within industry to overcome these limitations. It is shown the choice of U is critical to reproduce trends between materials as well as when any kind of quantititative agreement (e.g. for kinetic and thermodynamic studies) is needed. The final part of the talk will discuss our approaches to model different metal support interactions and the development of screening models to find optimal redox pairings of metal and support for catalytic applications.

COLL 437

Dynamics in surface chemistry
**Stephen J Jenkins, sij24@cam.ac.uk. Department of Chemistry, University of Cambridge, Cambridge, United Kingdom**

The prevalence of structural techniques in experimental and computational surface science inevitably encourages a static view of the atoms and molecules that make up the systems we study. Even discussion of chemical reactivity is most often couched in a quasistatic traversal of the minimum energy path between two local energy minima, or a high-level kinetic picture that emphasises the rate of passage from one minimum to another without enquiring too deeply into the mechanism by which that passage is effected. Nevertheless, we all know that at any finite temperature the atoms and molecules of interest will be in a state of constant agitation; even at the lowest temperature limit the phenomenon of zero-point motion is to be neglected at our peril. This talk will draw upon recent results from supersonic molecular beam and helium spin-echo studies, together with first-principles molecular dynamics simulations, to survey cases where a truly dynamic picture of the surface is essential to understand what is really going on. Examples include the partially dissociative adsorption of methane, the surface diffusion of pyrrole, and the anisotropic and anharmonic vibration of adsorbed glycinate molecules.

**COLL 438**

**Morphology of monolayer MgO films on Ag(100): Switching from corrugated islands to extended flat terraces**

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Oxide based materials are often used for relevant technological applications in fields as catalysis, corrosion protection, micro- and nano-electronics, sensoristics, spintronics, drug delivery, etc. The ability to engineer nearly perfect ultrathin oxide layers, up to the limit of monolayer thickness, is a key issue for nano-technological applications [1].

Here we face the difficult and important case of ultrathin MgO films on Ag(100), for which no extended and well-ordered layers could so far be produced in the monolayer limit. We demonstrate [2] that their final morphology depends not only on the usual growth parameters (crystal temperature, metal flux and oxygen partial pressure) but also on after-growth treatments controlling so far neglected thermodynamics constrains. We succeed thus in tuning the shape of the oxide films from irregular, nm-sized, monolayer thick islands (panel a), to slightly larger, perfectly squared bilayer islands (panel b), to extended monolayers (panel c) limited apparently only by substrate steps.
Panels (a-c): STM Images of MgO films of 0.7 ML nominal thickness grown under different conditions. SC and FC indicate slow and fast cooling, respectively. For all panels, image size 21x21 nm²; I=0.2 nA.

The combination of these parameters can be relevant not only for the production of oxide thin films but also for many other layered systems. Since the film structure influences both chemical and electronic properties of the layers, a full control of all experimental parameters opens important perspectives for applications in catalysis and for the use of ultrathin oxide films as support for the further deposition of organic and inorganic nano-objects.


COLL 439

Laser vaporization using ultra-fast, ultra-intense laser fields: From Newton’s cradle to mouse brain analysis

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The use of ultra-fast laser pulses to modify the Hamiltonian for molecules has enabled a series of new experiments due to the strong fields present. Examples from this laboratory include laser filamentation for remote detection, coherent control near conical intersections and new methods for nanomaterials synthesis. This contribution will focus on a new surface analysis experiment, the use of fs pulses to vaporize complex materials into the gas phase for ambient pressure mass analysis. The experiment has been performed to classify explosives, image narcotics, and analyze mouse brain. Laser vaporization has the ability to not only deliver macromolecules like proteins into the gas phase, but to preserve their tertiary structure. The talk will present an overview of the method, applications and mechanism of laser vaporization.

COLL 440

DFT study on selective CO₂ hydrogenation over the oxide supported metal clusters

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Catalytic conversion of CO₂ into liquid fuels and other value-added chemicals is a promising alternative to controlling CO₂ emission. Developing highly selective catalysts for CO₂ conversion becomes a focused research area in catalysis. In this talk, I will discuss our DFT computational results on CO₂ hydrogenation over the oxide supported metal clusters as model catalysts for CO₂ conversion. In particular, I will focus on the metal-support interface, which plays important roles in CO₂ hydrogenation.

COLL 441

Hydrogen bond fluctuations and time dependent infrared spectroscopy of aqueous solutions from first principles simulations

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We have employed a combination of theoretical methods such as ab initio molecular dynamics, population correlation function, time series analysis and nonlinear spectroscopic theories to investigate the dynamics of liquid water and aqueous solutions. In particular, we focus on time dependent transient absorption and multidimensional infrared spectroscopy of water and its relations to hydrogen bond fluctuations and other dynamical modes in aqueous medium. At room temperature, generally the dynamics is found to have a short time component that is attributed to dynamics intact hydrogen bonds and a slower longer time component that arises from breaking dynamics of hydrogen bonds and local structural relaxation. Effects of solute ions on the dynamics are also investigated. The current theoretical results are also compared with recent experiments on multidimensional infrared spectroscopy of water.
and aqueous solutions\textsuperscript{7,8}. Finally, preliminary results are also presented for nonlinear infrared spectroscopy of water at liquid-vapor interfaces from first principles simulations.

References:


**COLL 442**

**Computational studies of ions solvation with ring polymer molecular dynamics**

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To enhance our understanding of the mechanism of water-exchange around aqueous ions, we carried out systematic studies using Classical and Ring Polymer molecular dynamics simulations with empirical potential models. The mechanistic properties associated with the water-exchange process, such as ion-water potentials of mean force, time dependent transmission coefficients, and the corresponding rate constants, were examined using transition rate theory, the reactive flux method, and Grote-Hynes treatments of the dynamic response of the solvent. We also studied the effect of pressure on water-exchange rates and the corresponding activation volume. Our main research efforts will focus on understanding the influence of nuclear quantum mechanical effects on the properties of ions in aqueous solution such as the water-exchange rate and the corresponding transmission coefficients.
Recent applications of fluctuation solution theory

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Fluctuation Solution Theory (FST) provides relationships between the thermodynamic properties of a solution and the underlying pair distribution functions. Recently, we extended the theory to provide relationships between derivatives of the original thermodynamic properties and integrals over the triplet and quadruplet distributions. These relationships are used to extract the corresponding integrals from the existing experimental data for pure water and some binary solutions. The experimental data is complimented with molecular dynamics simulations of the solution mixtures. In particular, we investigate the effect of including explicit polarization in simulations of liquid water. A comparison of simulated and experimentally derived integrals is also performed and provides a quantitative way to assess the quality of current liquid state force fields.

Viscosity of aqueous electrolyte solutions: The dynamic point of view for hydrophobicity and hydrophilicity

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Hydrophobic and hydrophilic interactions are now relatively well understood as regards their origin and their thermodynamic and structural consequences. The dynamic aspect i.e. their influence on transport and time dependent properties are less familiar. For ions, colloids and particle in suspension, the key parameter is the solvation of the particle, explaining the variation of the hydrodynamic friction factor from 4 π to 6 π, for slipping to sticking particles. For the dynamics in porous materials a large variety of phenomena occurs, from electrokinetic phenomena to surface conductance, all related to the slipping (hydrophobic) or sticking (hydrophilic) character of the surface. As a result all details of interactions are required in order to explain quantitatively the observed phenomena. Dynamic properties appear then as a discriminative and severe test of theoretical models for surface interactions.

For the viscosity of electrolyte solutions, despite numerous efforts, no real progresses have been performed since the pioneering works by Debye, Huckel, Onsager and Falkenhagen. Contrary to further transport properties (such as the electrical conductivity or the diffusion coefficients), it is not possible to predict the viscosity of electrolyte
solutions beyond the limiting law from a microscopic point of view. The well-known Jones-Dole coefficient that characterizes the concentration dependance of the viscosity cannot be simply calculated from an extended Brownian model. Using Mode-Coupling Theory (MCT), we propose such an attempt, in the case of simple dissociated electrolyte solutions. We show that it is possible to quantify a breaking structure effect for the ions. Molecular dynamics indicate that this effect slightly depends on the nature of the ions. Then we propose a new simple model for the description of viscosity based on the MCT. It appears to be in agreement with experimental values for most of the simple electrolyte. The concentration dependance of viscosity appears to be a subtle consequence of opposite effects: Coulombic forces, solvent structure breaking, hydrophobicity and hydrophilicity.

**COLL 445**

**Water-mediated molecular and ionic interactions**

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Water mediated interactions between hydrophobic and ionic group are investigated using both vibrational spectroscopy and molecular dynamics simulations. Experimental hydration-shell vibrational spectra are obtained by combining Raman spectroscopic measurements with a multivariate curve resolution (Raman-MCR). The results are used to probe the structure of the hydration shells of carboxylic acids with either charged on neutral head groups, and hydrophobic tails of various sizes. Our combined experimental and molecular dynamics simulation results illuminate the coupling between hydrophobic and ionic water-mediated interactions, as charging the carboxylic acid head group influences the neighboring hydrophobic hydration shell structure.

**COLL 446**

**Metal ion binding at the active site of DNA polymerases**

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Metal ions play an integral role in enzymatic reactions and about third of the enzyme mediated processes are controlled by metal ions. DNA polymerases that are critical for genome integrity and stability are assisted by divalent metal ions in carrying out their functions of repair or replication. In DNA repair, two magnesium ions are required at the active site of the repair enzymes, DNA polymerases. One metal ion is bound to the incoming nucleotide triphosphate (the nucleotide binding metal) whereas the second metal ion helps prepare the O3’ of the primer terminal for nucleophilic attach (the catalytic metal). The final event before the chemical step is speculated to be the occupation of the catalytic metal ion at the catalytic metal site. We have carried out a
series of molecular dynamics simulations to study the assembly of two divalent metal ions at the active site of the DNA polymerase beta. The results are discussed in terms of the ion hydration under various conditions.

**COLL 447**

**Lipid bilayer-nanoparticle interactions probed by second harmonic and vibrational sum frequency generation**

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The interaction of nanoparticles with supported lipid bilayers is studied by nonlinear optics.

**COLL 448**

**Influence of natural organic matter on the interaction of functionalized nanoparticles with supported lipid bilayers**

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The growing use of nanotechnology has led to increased interest in understanding the molecular-level interactions of nanoparticles in environmental matrices. Natural organic matter (NOM) can form an "environmental corona" around the nanoparticle and impact nanoparticle hydrodynamic and electrokinetic properties, but the effects on subsequent biological interactions are poorly understood. We have conducted studies aimed at understanding how nanoparticles functionalized with different surface ligands interact with NOM and how the presence of NOM impacts nanoparticles interaction with solid-supported lipid bilayers (SLBs), a model for cellular membranes. We characterize the interaction of NPs with supported lipid bilayers in real time in the presence and absence of NOM using quartz crystal microbalance with dissipation monitoring. NOM-induced changes in hydrodynamic size were measured using dynamic light scattering, and changes in charge were investigated using laser Doppler microelectrophoresis. Our studies show the presence of NOM decreases the attachment of positively charged diamond nanoparticles to SLBs composed of zwitterionic phospholipids or mixtures of zwitterionic and negatively charged phospholipids. Contrary to initial expectations based on simple electrostatics, we observe that positively charged nanoparticles bind to a larger extent to a purely zwitterionic bilayer compared to a mixed bilayer in which zwitterionic molecules are mixed with negatively charged molecules. Our results show
that nanoparticle interactions with SLBs involve a complex interplay of interactions. We will discuss these and other studies aimed at elucidating the molecular-level interactions of nanoparticles with SLBs.

**COLL 449**

**Nanoparticle “insertion” into anionic and phase separated lipid monolayers**

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Dynamic surface pressure measurements, coupled with optical and electron microscopy, are used to examine interactions between lipid membranes and engineered nanoparticles as a function of nanoparticle concentration and surface charge, and membrane composition and interfacial tension. This approach is reminiscent of that for peptides or proteins, where their interactions with lipid monolayers have been described based on a maximum “insertion” pressure (MIP). The objective is to develop an approach that can detect the kinetics of nanoparticle binding and membrane reorganization, and to test the MIP concept for engineered nanoparticles. Saturated dipalmitoylphosphatidylcholine (DPPC, zwitterionic) and dipalmitoylphosphatidylglycerol (DPPG, anionic), and unsaturated dioleoylphosphatidylcholine (DOPC, zwitterionic) and dioleoylphosphatidylglycerol (DOPG, anionic) are used to form single or mixed monolayers at air/water interfaces with varying biophysical structure and phase behavior. Anionic glycerol lipids are used to create model bacterial membranes, and silver nanoparticles with charged or neutral organic surface coatings are used because of their biological relevance (e.g. antibacterial properties). Our initial results have shown that interactions are primarily dependent upon the degree of electrostatic and hydrophobic interactions, and the intermolecular spacing between the lipids. At low initial surface pressures (~10 to 15 mN/m), cationic nanoparticle binding leads to a large increase in surface pressure that takes place over many hours. In contrast, at high initial surface pressures (> 15 mN/m), there is a small increase in surface pressure over a much shorter length scale. These differences reflect changes lipid packing and mobility, and the lipid-condensing effect the nanoparticles have at the air/water interface. Additional studies are underway to determine the effects of salts and to determine how proteins competitively bind to modulate interactions.

**COLL 450**

**Functionalization of fully disaggregated nanodiamond for study of fundamental particle-environmental interactions**

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Materials at the nanoscale are known to affect biological systems. To understand how particles act in the environment at a molecular level, well controlled particle systems are necessary. We have chosen nanodiamond as a model system to understand the factors that govern nano-bio interactions at a molecular level, because the covalent functionalization of diamond leads to surfaces with unprecedented chemical stability. Full disaggregation and concomitant functionalization methods have been optimized to create a library of dispersed nanoparticles that have tunable properties (e.g. charge and ligand bonding architecture). Control over diamond serves to match similar chemistries on gold nanoparticles, allowing the ability to elucidate the effect of particle functionality against core type. In probing molecular based interactions, we have been careful to rigorously quantify ligand density by X-ray Photoelectron Spectroscopy, applying particle curvature corrections to obtain meaningful values. The culmination is to have control over the core and ligand to understand the importance of each on the final particle's properties.

**COLL 451**

**Surface chemistry of environmentally and biologically relevant molecules on nanoparticle surfaces and its impact on interactions with natural and engineered interfaces**

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This talk will focus on the adsorption of environmentally and biologically relevant molecules on the surface of metal oxide nanoparticles. The application of ATR-FTIR spectroscopy to study surface adsorption, delineate surface structure, quantify surface coverage and determine thermodynamic equilibrium constants is shown. Furthermore, because surface adsorption changes surface charge and hydrophobicity, it will alter nanoparticle interactions with natural and engineered interfaces, as will be discussed.

**COLL 452**

**Interaction of engineered and natural nanoparticles (NPs) at solid-water, solid-organic matter, and solid-microbe interfaces**

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We have studied the interaction of engineered and natural NPs, including Ag(0), ZnO, CuO, and 2-line ferrihydrite (2L-Fh), with aqueous solutions, natural organic matter (NOM), and E. coli bacteria, to understand their transformations and reactivity in complex natural environments. Engineered Ag(0) NPs commonly coated by polyvinylpyrrolidone (PVP) are readily transformed to Ag2S and AgCl NPs or aqueous Ag-Cl species when exposed to aqueous solutions containing inorganic sulfide and chloride ions, respectively. Using solubility measurements, XPS, TEM, and high energy synchrotron x-ray total scattering and pair distribution function analysis, we found that PVP-coated Ag(0) NPs transform to Ag2S, forming a core-shell structure, which results in significantly lower release of Ag+ ions and thus lower toxicity to a variety of organisms. ZnO NPs when exposed to sulphide in aqueous solutions forms ZnS NPs; the transformation mechanism is dissolution followed by re-precipitation which differs from that for Ag(0) NP sulfidation. When exposed to inorganic sulphide CuO transforms to CuS, which results in higher release of Cu2+ to solution and higher toxicity. 2L-Fh NPs from acid mine drainage environments are often associated with NOM and high concentrations of Al and Si. We used the same methods as above in addition to 27Al NMR and STXM to study the structure and strain of 2L-Fh NPs and their interactions with Si and Al and found that Al can substitute for Fe3+, whereas no observable substitution of Si into Fh structural sites was found. We have also found that synthetic 2L-Fh (Fe_{8.2}O_{8.5}(OH)_{7.4}3H_2O) transforms to a more ordered form of different stoichiometry (Fe_{10}O_{14}(OH)_{2}•1H_2O) and ultimately to hematite (alpha-Fe_{2}O_3) when exposed to citrate at elevated temperature (175°C). The effects of NOM coatings on the reactivity of 2L-Fh were examined by EXAFS studies of Zn(II)- and U(VI)-reacted 2L-Fh with and without NOM coatings and will be reviewed.

COLL 453

Single nanoparticle surface plasmon resonance microscopy of DNA hybridization adsorption and surface polymerization

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The bioaffinity adsorption of single biofunctionalized nanoparticles onto chemically modified gold thin film surfaces was measured in real time with near-infrared surface plasmon resonance (SPR) microscopy1. A 814 nm objective-coupled, high numerical aperture SPR microscope was used to detect the changes in the SPR reflectivity image due to the adsorption of single gold, polystyrene, or hydrogel nanoparticles with diameters ranging from 500 to 20 nm over a 85 x 85 micron image area. Diffraction of the surface plasmon polariton waves traveling across the gold surface by the adsorbed nanoparticles resulted in a very large oscillatory response in the SPR image. Quantitation of this unique optical response allowed us to monitor the adsorption and desorption of nanoparticles with sub-micron spatial resolution with a time resolution of 1 s over 10 min. The resultant SPR image movies were used to monitor the hybridization adsorption of DNA-functionalized nanoparticles at sub-picomolar concentrations, the accumulation of DNA-functionalized nanoparticles onto enzymatically synthesized
surface RNA sequences, and the sensitivity of hydrogel nanoparticles to changes in buffer composition and hybridization adsorption stringency.

Reference:


**COLL 454**

**Stimuli-responsive polymersomes for cytosolic drug delivery to cancer cells**

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Liposomes are frequently used as carriers of drugs and imaging agents. Although several successful targeting strategies are reported, the liposomes suffer from a lack of stability and slow release of the encapsulated contents at the targeted site. Polymersomes are bilayer structures formed from amphiphilic polymers in aqueous media. These vesicles are considerably more stable compared to liposomes; however, they also demonstrate a slow release for the encapsulated contents, limiting their efficacy as a drug-delivery tool. As a potential solution, we have successfully prepared
echogenic, redox-sensitive, targeted polymersomes. Ultrasound-scattering and imaging experiments confirmed the echogenicity of the vesicles. These polymersomes showed excellent release profiles when incubated with cytosolic concentrations of reducing agents, releasing more than 80% of the contents within 20 minutes. However, in serum levels of reducing agents, minimal release was observed. When a folate lipid was incorporated in the bilayer, the polymersomes showed an enhanced uptake with folate-receptor overexpressing breast- and pancreatic-cancer cells. A combination of the two anticancer drugs, gemcitabine and doxorubicin, was successfully encapsulated in the polymersomes. These targeted, dual-drug encapsulating polymersomes significantly decreased the viability of breast- and pancreatic-cancer cells in the monolayer as well as in spheroid cultures. Our results are expected to encourage further research about the use of ultrasound-reflective polymersomes as multimodal drug carriers with targeting and triggered release properties.

COLL 455

High-throughput formulation of nanoparticles and polyplexes for structure-property investigations

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High-throughput (HT) experimentation represents a fast and efficient tool for the preparation and characterization of materials for diverse pharmaceutical applications such as basic structure-property relationships of polymers and their drug and gene delivery potential. Influencing factors for the formation of polymeric nanoparticles by nanoprecipitation can be analyzed in a fast and efficient manner by using liquid handling robots and HT-DLS. We show that the polymer molar mass as well as polymer-solvent interactions have a significant influence on the nanoprecipitation behavior. A further application field is a HT workflow for gene delivery in vitro. In detail, complex preparation (polymer and genetic material), complex size, DNA binding affinity, complex stability, cytotoxicity, and transfection efficiency can be investigated via HT-assays. To proof the usage of the investigated workflow, various poly(ethylene imine)s (PEI) of linear and branched architecture and different molar masses as well as plasmid DNA as genetic material were used as representative polymer and genetic material, respectively.

This approach allows the testing of many different polymers and parameters concerning biological outcomes as transfection properties or cytotoxicity, and yields faster insights into structure–property relationships for biological activity.

Figure 1. Schematic representation of the HT preparation and screening of polyplex formulations.
Precisely tunable engineering of sub-30 nm monodisperse oligonucleotide nanoparticles

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Advancement of RNAi therapies is mainly hindered by the development of efficient delivery vehicles. The ability to create small size (< 30 nm) oligonucleotide nanoparticles is essential for many aspects of the delivery process but is often overlooked. In this report, we describe di-block star polymers that can reproducibly complex double-stranded oligonucleotides into monodisperse nanoparticles with 15, 23 or 30 nm in diameter. The polymer-nucleic acid nanoparticles have a core-shell architecture with dense PEG brush coating. We characterized these nanoparticles using ITC, DLS, FRET, FCS, TIRF and TEM. In addition to small size, these nanoparticles have neutral zeta potentials making the presented polymer architecture a very attractive platform for investigation of yet poorly studied polyplex size range for siRNA and antisense oligonucleotide delivery applications.

Self-assembled polymer drug carriers for rational combination and RNA interference therapy of solid tumors

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Drugging solid tumors with small interfering RNA and rational combinations of molecularly targeted therapeutics can be difficult to achieve using traditional pharmaceutical excipients and drug carriers. Self-assembled polymer nanoparticles represent a powerful tool that can tailor the delivery of a specific drug or drug combination in a manner that maximizes synergistic or synthetic lethal interactions while minimizing toxicity. Here, we describe the development of a hierarchically-assembled polymer drug carrier that targets solid tumors through three independent mechanisms and its use to drug breast tumor xenografts through synergistic horizontal blockade of oncogene-addicted and resistance-associated cell signaling. We also describe the
development of a series of lipid-like polypeptides that can be used to deliver small interfering RNA against a novel DNA damage signal effector whose loss is synthetic lethal in the absence of functional tumor suppressor protein p53. These strategies directly address unmet needs in current clinical therapies for breast, lung, and ovarian cancer.

COLL 458

Morphological dependence of biodistribution and clearance rates on MR-contrast agent labeled polymeric nanomaterials

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Nanoscale materials can be manipulated for a variety of uses in matters pertaining to nanomedicine, specifically \textit{in vivo} targeting of materials. A novel norbornene-based analogue of a gadolinium-containing small molecule contrast agent (Gd-DOTA) was polymerized to form the hydrophilic component of water-soluble or amphiphilic block copolymers. We synthesized a small library of gadolinium-containing polymers using ring-opening metathesis polymerization. Different ratios of hydrophilic-to-hydrophobic block copolymers allowed access to spherical micellar nanoparticles or fibromicellar structures, with the gadolinium-containing block displayed as the shell of the particle. A hydrophilic polymer, completely dispersed in water, was synthesized in the same manner. Subsequent nanoparticle formulation following ROMP allowed us to synthesize chemically similar materials with dramatically different nanoscale morphologies: either dispersed polymers, micellar nanoparticles, or fibromicellar nanoparticles in an aqueous environment. The effects of morphology \textit{in vivo} were studied via intraperitoneal injection of materials in to C57B1/6 mice. Real-time imaging of mice were performed using a 7T MRI instrument. $T_1$ analysis of the bladder showed clearance of the small-molecule and polymeric materials within 2 hours. Nanoparticles, on the other hand, showed limited clearance via the bladder, while qualitative analysis showed considerable retention of these materials in the IP space several hours after injections. For all materials, complete clearance was observed after one week. Extended retention in the IP space and full clearance of nanomaterials one week post-IP injection has implications for treatment of peritoneal cancers.

COLL 459

Polymer-based design of multifunctional liposomes for cancer therapy
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Liposomes are considered as ideal carriers for drugs and bioactive molecules, because of their encapsulation ability and biocompatible properties. To increase their usefulness, we developed two types of multifunctional liposomes by incorporating functional components into liposome membranes. We incorporated temperature-sensitive block copolymers, gadolinium chelate-attached dendron lipid and target specific ligands such as transferrin and cRGD peptide into liposomes. Incorporation of temperature-sensitive block copolymer having a phase transition temperature of about 40 °C into stable liposomes consisting of egg yolk phosphatidylcholine and cholesterol afforded highly temperature-responsive liposomes which released content above 40 °C. Incorporation of gadolinium chelate-attached dendron lipid into the liposome membranes enabled their detection in the body with MRI. In addition, incorporation of ligands to the liposomes modified biodistribution. The MRI analysis showed that conjugation of transferrin did not improve the tumor accumulation of the liposomes but the attachment of cRGD enhanced liposome accumulation in tumor. Because cRGD has high affinity to integrin which is overexpressed on endothelial cells of tumor capillaries, their specific interaction might enhance accumulation of the liposomes in the tumor tissue. These ligand-attached temperature-responsive liposomes were loaded with doxorubicin and examined their tumor suppressive effects. These liposomes were administered to colon26 tumor-bearing mice from the tail vein and the tumors were heated at 44°C for 10 min 8 h after the liposome administration. The liposomes with cRGD exhibited stronger tumor suppressive effects than those with transferrin. Probably, efficient accumulation of the liposomes with cRGD might result in the excellent therapeutic effect. We also prepared multifunctional liposomes that deliver antigenic proteins into dendritic cells and activate them at the same time by incorporating both pH-sensitive polymers and adjuvant molecules into liposome membranes. When injected into tumor-bearing mice, these liposomes induced tumor specific immunity, which caused tumor suppression effectively.

COLL 460

X-ray scattering from tetrapod-shaped DNA in aqueous solution to determine its structures relating to biological activity

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We carried out synchrotron small-angle X-ray scattering (SAXS) from four types of tetrapod-shaped DNA (DNA tetrapod) with different sequence but the same number of total base pairs, containing an immunostimulatory CpG motif and confirmed that indeed they forms the expected tetrapod-shape. The sample with the larger radius of gyration ($R_g$) induced the more cytokine secretion in vivo. Structural analysis combining with computational simulation and a simple tetrapod rigid body model revealed that the larger $R_g$ is ascribed to dissociation of the DNA double strands at the central connecting part of the DNA tetrapod. From this finding, the biological activity is related to how easily the single DNA strands can be formed, which is consistent with the fact that the CpG receptor TLR9 can only bind single strands of DNA.

**COLL 461**

**Polymersomes platform for cancer therapy**

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Appropriate and effective delivery is vital to a drug's therapeutic success. In order for a drug to exert its therapeutic effect, it must be delivered to the target cells, at the optimum dose and in its active form. Drugs delivered inappropriately to healthy tissues and organs can produce off-target effects resulting in suboptimal or even abandoned treatment. The past decade has seen a dramatic increase in research into the use of various nanoparticles to deliver therapeutic agents to overcome some of these challenges. Synthetic polymers are showing great promise particularly in recent years where liposome and polymer technology have merged in the design of self-assembling membrane-enclosed structures comprising block copolymers called polymersomes. In this work we present the efficient and stable encapsulation of doxorubicin and taxol or the combination of the two within pH sensitive polymersomes as multi-(intra)-cellular delivery platform. PMPC$_{25}$-PDPA$_{70}$ polymersomes have been prepared using film rehydration. TEM, DLS, HPLC and dialysis chamber were used to characterize the polymersomes structure, loading efficiency and retention efficiency respectively. Polymersome uptake and ability to deliver encapsulated drugs into healthy normal cells and cancerous cells was measured in two and three-dimensional culture systems. In monolayer culture, only a short exposure to drug-loaded polymersomes was required to elicit a strong cytotoxic effect. When delivered to three-dimensional tumor models, the polymersomes were able to penetrate deep into the center of the spheroid resulting in extensive cell damage when loaded with both singular and dual-loaded chemotherapeutics. Furthermore, polymersome cellular uptake was discovered to be enabled by class B scavenger receptors. What was also observed was that these receptors are more highly expressed by cancer cells compared to normal cells. This
indicates that PMPC-PDPA polymersomes offer a novel platform for the effective delivery of chemotherapeutics for cancer treatment. Moreover, the preferential internalization of PMPC polymersomes by exploiting elevated scavenger receptor expression on cancer cells opens up the opportunity to a polymersome-mediated targeting to tumors.

OPTIMIZING TOBACCO MOSAIC VIRUS RODS AND SPHERES FOR MRI DETECTION OF ATHEROSCLEROTIC PLAQUES

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Atherosclerosis, inflammation of the arteries, is the underlying cause of most deadly cardiac events, such as strokes and heart attacks. Early and non-invasive diagnosis of atherosclerotic plaques will lead to better patient outcomes. To accurately detect plaques vulnerable to rupture, molecular imaging is required. Magnetic resonance imaging (MRI) provides the high spatial resolution and soft tissue contrast required to detect molecular markers on atherosclerotic plaques. Molecular MRI, however, requires high contrast agent accumulation due to its inherent low sensitivity. Nanoparticles are ideal platforms for cargo delivery, including contrast agents and therapeutics, because they can deliver large payloads to specific cells and tissues. We have turned toward the nanoparticles derived from plant viruses. Viral nanoparticles provide an excellent platform for cargo delivery because they are capable of chemical and genetic modification, easily attainable in various shapes and sizes, and designed by nature to deliver cargo to cells. Tobacco mosaic virus (TMV) presents a rod-shaped platform measuring 300 x 18 nm. TMV is capable of undergoing thermal transition to form spherical nanoparticles (SNPs), thus affording us the ability to test the structure-function relationship of targeting molecular markers under the unique physiological environment of atherosclerotic plaques. We have shown that covalent attachment of paramagnetic contrast agents, chelated Gd(DOTA), to TMV rods and spheres increases the ionic relaxivities of the agent. Mineralization of the Gd(DOTA)-modified TMV templates further increases the ionic relaxivity of Gd ions. In this presentation, we will discuss the engineering principles leading to TMV-based MRI contrast agents for detecting molecular markers on atherosclerotic plaques.
PRINT microneedles for the transdermal delivery of therapeutics

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Many microneedle-based drug delivery systems require long fabrication times and are not easily scalable, hindering the advancement of biodegradable microneedles. We have fabricated reproducible polymeric microneedles via Particle Replication in Nonwetting Templates (PRINT®) technology, an easily scalable roll-to-roll process invented our laboratory. Microneedle masters were developed using a tilted UV photolithography approach; a positive replica was then used to make PRINT-compatible molds from a photocurable perfluoropolyether (PFPE) elastomer. The molds, which are non-wetting, non-swelling, and gas permeable due to the highly fluorinated PFPE, were then used to create arrays of discrete microneedles on flexible, water-soluble substrates. This flexibility allows the array of highly-dense microprojections to avoid the “bed of nails” effect and break the stratum corneum more efficiently. Microneedle devices of this nature could be applicable for the delivery of many therapeutic cargos, including small molecules, proteins, and nano- and micro-particles. In addition to vaccines or routine injections, PRINT microneedles may also be used for the treatment of breast cancer, specifically inflammatory or chest wall recurrent breast cancer. Unlike many breast cancers that present as a lump, these dysplastic cells commonly reside in the dermal lymphatics. As innovative strategies are critical, a novel transdermal-based approach could serve as an avenue for a local and possibly systemic, yet minimally invasive, therapy. Recently, PRINT microneedles loaded with docetaxel, and anti-mitotic chemotherapeutic currently used for the treatment of locally advanced breast cancer, have been fabricated at a variety of loadings. These reproducible, homogenous microneedle patches will be used in pre-clinical models to study the efficacy the chemotherapeutic via this route of administration.

IVT2H-drop based single cell protein analysis

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We combine drop-based microfluidics and an IVT2H system to develop a drop-based IVT2H platform; this platform enables cost-effective, fast, high-throughput, label-free, and stress free protein detection at a single-cell level. We demonstrate this capability by
quantifying antibodies in single antibody-secreting cells and detecting kinase activity in single cancer cells. These can be directly applied to construct engineering antibody, test drug efficiency, and enrich drug-resistance cells. More broadly, because IVT2H system can be potentially designed to detect many types of proteins as long as two binding molecules are available for this protein, thus, our technique can be a universal method to assay proteins within single cells. Moreover, the ability to link genotype and phenotype of single cells enables investigation of the relationship between protein level change and the changes at both genomic and transcriptomic levels; this will strongly deepen the understanding of a highly heterogeneous cell population, and thus provide a powerful tool to study the rare but significant biological events and design customized strategy for cancer diagnosis and treatment.

COLL 465

Cellulosic coatings for stabilizing oxide particle dispersions

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Polymeric surfactants and coatings are crucial technologies for stabilizing particle dispersions and tuning their colloidal interactions in paints, consumer products, and biomaterials. Cellulosic polymers offer sustainability benefits and diverse derivatization options for tuning the surface chemistry of particles. This presentation will report the preparation of multilayer coatings from cellulosic polymers on inorganic oxide particles via a novel single-pot method. The surface chemistry of this cellulosic coating compared to traditional polyelectrolytes will be discussed with particular emphasis on stabilizing paint formulations.

COLL 466

Atomic force microscopy and lithography of mercaptoalkanoic acid "molecular ruler" multilayers

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Complex surface structures with molecular-scale organization and chemical functionality have garnered tremendous attention in recent years for applications including biocompatible surfaces and molecular-scale lithographic resists. Alkanethiol-based chemical films assembled onto Au surfaces are commonly utilized for these applications. However, the majority of alkanethiol-based fabrication strategies only create two-dimensional surface architectures due to their reliance on the assembly of monomolecular films. One strategy to generate three-dimensional chemical films utilizes
the sequential deposition of mercaptoalkanoic acid molecules and coordinated metal ions where the overall film thickness of the multilayer film is governed by the number of iterations in the deposition process. We have combined this multilayer assembly strategy with nanoshaving to characterize and to manipulate the local structure of these multilayer films. Nanoshaving is a type of atomic force microscopy lithography that utilizes an atomic force microscopy tip to displace adsorbed molecules from a surface to reveal the underlying Au substrate. The local thickness and surface morphology of these multilayer films will be investigated. Further, we will demonstrate that various layers of the multilayer film can be removed by tuning the nanoshaving force. This combination of molecular assembly and scanning probe lithography illustrates a general approach to generate three-dimensional chemical films with varied surface chemistries.

**COLL 467**

**Adsorption of a polyelectrolyte-surfactant complex at an aqueous-solid interface**

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The strong association between polyelectrolytes and oppositely charged surfactants, governed by coulombic and hydrophobic interactions, leading to an idiosyncratic bulk phase behavior of the complex, has been well studied. A few interfacial studies have investigated the effect of sodium dodecyl sulfate (SDS) on the pre-adsorbed cationic polymer and also the adsorption from premixed cationic polymer/SDS complex over anionic silica, using techniques such as ellipsometry. However, limited information was obtained by ellipsometry for pre-mixed polymer/surfactant systems, which are technologically more relevant, because solutions are turbid in a range of SDS concentration. In our studies, we used the quartz crystal microbalance with dissipation (QCMD) technique to quantify the adsorbed mass of the pre-mixed quaternized hydroxyethyl cellulose ethoxylate (PQ10)/SDS complex and to qualitatively predict the conformation of the adsorbed complex on the amphoteric surface of Al₂O₃. We found that with increasing SDS concentration the adsorbed mass continued to increase, resulting in an increased loop conformation. Moreover, maximum adsorption was observed just before the phase separation on both negative and positive surfaces. Premixed polymer/SDS solution at high SDS concentration upon dilution, during rinsing, led to an increase in adsorption, an observation reported earlier. However, we found this to be true only on the negative surface and not on the positive surface. Using zeta potential, streaming potential, and QCMD to systematically analyze the parameters critical for polyelectrolyte adsorption, we found that controlling the net charge on the PQ10/SDS complex is crucial for optimum adsorption. We also present spectroscopy results to identify the adsorbed species from the multicomponent system.

**COLL 468**

**Engineering of monolayers and bilayers at an aqueous microdroplet**
Amphiphilic molecules spontaneously self-assemble into ordered nanostructures at the
liquid-liquid interface. This presentation will feature how the soft surface of an aqueous
microdroplet can be engineered to modulate the key properties of the surface using
amphiphilic molecules. In turn, the interfacial surface of the droplet can be employed to
influence the formation of a microparticle within the droplet, through templated
nucleation. We will show that the use of self-assembled monolayers of various
surfactants and other biological lipids having various molecular shape can influence the
surface properties of the monolayer and bilayer. In addition, the subtle characteristic
interactions between the droplet content and the self-assembled structure at the
monolayer and bilayer will be shown to have a remarkable difference in its packing
arrangements and permeability. The successful demonstration of soft surface
engineering at the micron size level will play a significant role in predicting and allowing
to control the final nanostructure formed by amphiphilic systems.

COLL 469

Surface modification by adsorption and co-adsorption of charged or nonionic
polymer brush nanoparticles

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Polymer brush nanoparticles are highly curved polymer brushes that are designed to be
dispersed in a good solvent. They share the core/corona architecture of block
copolymer micelles formed in a selective solvent, but they are distinguished from
micelles by their inability to disassemble. Polymer brush nanoparticles can take the form
of polymer brushes grafted from rigid, initiator-functionalized core nanoparticles or multi-
arm star polymers with cross-linked polymer cores. Often, a polymer brush nanoparticle
has a core radius that is comparable to the brush thickness. Polymer brush
nanoparticles may prove to be particularly interesting surface modification agents. We
previously demonstrated that their adsorption behavior at oil/water interfaces makes
them extremely efficient and effective emulsifiers. The current work focuses on their
adsorption to solid/liquid interfaces, as we also envision their use as wetting agents,
dispersants or boundary lubrication agents. This presentation considers adsorption of
polyelectrolyte brush-grafted nanoparticles and nonionic star polymers from aqueous
suspensions to solid surfaces. The polyelectrolyte system consists of the weak cationic
polyelectrolyte poly(2-(dimethylamino)ethyl methacrylate) grafted from silica
nanoparticles (PDMAEMA-SiO₂) by surface-initiated atom transfer radical
polymerization (ATRP). The nonionic system consists of poly(ethylene oxide) star
polymers (PEO stars) prepared by ATRP of poly(ethylene oxide) methacrylate
macromonomer in the presence of divinylbenzene cross-linkers. These are adsorbed to silica surfaces from aqueous suspensions. The simultaneously acting effects of electrostatic attraction to the surface and electrostatic repulsion among neighboring particles makes PDMAEMA-SiO$_2$ adsorption highly sensitive to pH and ionic strength. Hysteretic adsorption effects allow the extent of adsorption and the structure of the adsorbed layer to be processed by sequential changes in pH. Under normal adsorption conditions, electrostatic repulsions among individual PDMAEMA-SiO$_2$ particles leave unfilled gaps on the surface. PEO star adsorption, on the other hand, fills the surface more completely. Co-adsorption of PEO stars and PDMAEMA-SiO$_2$ produces high surface coverage layers that are mainly nonionic but are doped with discrete positively charged PDMAEMA-SiO$_2$. Ellipsometry, quartz crystal microbalance with dissipation and streaming potential measurements are conducted to characterize the amount of adsorption, and the composition, charge and dynamic properties of the adsorbed layers. Colloidal probe atomic force microscopy measurements of normal and lateral surface forces between opposing layers are performed to determine layer compositions that provide strongly repulsive long range normal forces with diminished adhesion on contact and lessened frictional forces.

**COLL 470**

**Adsorption of cationic nanosized particles on natural fiber for hydrophobic modification**

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The barrier resistance against water vapour transfer is of great importance. In this work, core-shell latexes based on butyl acrylate (BA), 2-ethylhexylacrylate (EHA) and methyl methacrylate (MMA) using cetyl trimethyl ammonium bromide (CTBA) as a cationic surfactant were prepared via a seeded emulsion copolymerization. The latex or colloidal particles were applied to paper either as wet-end additive or coated layer in an attempt to improve hydrophobicity. It was found that both approaches increased the hydrophobicity of the fibre networks (demonstrated by the increasing of contact angles); and the hydrophobic enhancement is proportional to the amount of the latex added. For the wet-end addition, the adsorption of the nanosized particles on natural or cellulose fibers play an critical role in the modification or rendering fiber network hydrophobic. The cationic surfactant on the latex surface ensured its high retention with cellulose fibers. SEM images confirmed that upon heating, the hydrophobic film was formed in fiber networks due to the low glass transition temperature $T_g$ of the nanoparticles which pre-adsorbed on the surfaces of fibers. However, the improvement in lowering water vapor transfer rate (WVTR) induced by the latex added at wet-end was limited, implying that the hydrophobic modification does not necessarily lead to extremely low WVTR.
However, the wet-end addition in conjunction with coated layer indeed improved the hydrophobicity of paper and meanwhile reduced WVTR.

COLL 471

Cyclic azasilanes: A new generation of efficient silane coupling agents

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Organofunctional substituents and inorganic surfaces are frequently linked using a variety of silane coupling agents. Common categories of silane-coupling agents include alkoxy and chlorosilane based materials, which are used in nanoparticle treatment, microelectronics, and other surface modification applications. Despite their versatility, these two groups of silane coupling agents release alcohol or hydrochloric acid upon reaction with the surface. Furthermore, additional byproducts can adhere to the substrate surface because of the requisite hydrolysis step prior to reaction with the surface when using alkoxy silanes specifically. Cage-like silane condensation products have previously been observed, potentially affecting the targeted chemical properties.

Cyclic azasilanes afford efficient and atom economical alternatives to conventional silane coupling agents. With these coupling agents, hydrolysis is not needed, as ring opening through the cleavage of the inherent Si-N bond in these structures, promotes both a strong attachment to surface hydroxyl groups as well as releasing no byproducts during attachment. The HCl and alcholic byproducts so commonly released using conventional silane coupling agents are eliminated using these new efficient cyclic azasilanes, thereby reducing the overall waste stream. Furthermore, reaction with surface hydroxys occurs in a fraction of the reaction time (generally less than one minute) compared to that of the conventional silane-coupling agents. The synthesis, characteristics, and applications of cyclic azasilanes as coupling agents and additives will be presented. Conventional silane coupling agents and cyclicazasilanes will be compared. The surface interaction, topography, and durability of the monolayer supported by $^1$H NMR, kinetics, FTIR, XPS, AFM, and ASTM testing will also be presented.

COLL 472

Understanding polyelectrolyte assembly at oil-water interfaces: Challenges and progress in combining computation and surface spectroscopy

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How polyelectrolytes in the presence of various additives assemble at an oil-water interface is important to a variety of applications. While experiments using surface spectroscopy are making significant inroads into understanding these complex systems,
it is increasingly clear theoretical calculations are required to develop a full picture. Classical molecular dynamics with a polarizable force field is used to investigate changes in structure for two diastereomers (isotactic and syndiotactic) of a methacrylic acid polymer (PMA) in the presence of different additives. Additionally, vibrational sum-frequency spectra are calculated to determine what spectral changes accompany changes in structure for future comparison with experiment. The computational spectra are determined using the conformations and orientations from the molecular dynamics calculations and vibrational and response properties from density functional calculations. The calculated spectra provide a direct link to experimental measurements helping to show the accuracy of the calculated behavior.

**COLL 473**

**Surface modification of transparent conducting oxides with functionalized perylene diimide dyes: Characterization of orientation, charge-transfer kinetics, and related OPV performance**

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Charge transfer efficiency at the organic/electrode interface is one of the key parameters controlling the overall efficiency of organic photovoltaics (OPVs). Modification of this interface with a redox-active organic surface modifier may enhance the charge transfer across the interface by providing a facile charge-transfer pathway between the electrode and the organic active layer. Using two functionalized perylene diimide (PDI) molecules with different linkers to a phosphonic acid (PA) anchoring group, three different PDI sub-monolayer films were deposited onto indium tin oxide (ITO) surfaces (self-assembled PDI-phenyl-PA film, self-assembled PDI-diphenyl-PA film and spin-coated PDI-phenyl-PA film) to study the relationship between molecular structure, the charge transfer rate constants at the ITO surfaces and related OPV performances. Polarized attenuated total reflectance spectroscopy (polarized-ATR) shows that PDI films deposited using self-assembly are predominately out-of-plane with average tilt angles between the molecular axis and the surface normal of 33° for self-assembled PDI-phenyl-PA films and 31° for self-assembled PDI-diphenyl-PA films, while films deposited using spin-coating are more in-plane with an average tilt angle of 45°. Potential-modulated attenuated total reflectance (PM-ATR) measurements show that the spin-coated PDI-phenyl-PA film has an apparent rate constant ($k_{s, app}$) of $5 \times 10^4 \text{ s}^{-1}$ for the first electron reduction/oxidation process. The self-assembled PDI-phenyl-PA film
has an $k_{\text{app}}$ of $1.4 \times 10^4 \text{ s}^{-1}$ due to its more out-of-plane orientation compared to the spin-coated film, while the self-assembled PDI-diphenyl-PA film has the lowest charge transfer rate constant of $0.5 \times 10^4 \text{ s}^{-1}$ as a result of its longer linker group compared to the PDI-phenyl-PA molecule. P3HT/PCBM bulk-heterojunction inverted organic photovoltaics (OPVs) were also fabricated on top of the PDI films on ITO. The power conversion efficiencies are higher than the OPVs fabricated on bare ITO surfaces.

**COLL 474**

**Adsorption of “soft” spherical particles onto sinusoidally-corrugated surfaces**

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We utilize a Monte Carlo simulation scheme based on the bond fluctuation model to simulate settlement of "soft" adhesive particle onto sinusoidally-corrugated surfaces. Particles are composed of a hard inner core with a "soft" adhesive shell made of surface grafted polymer chains. These chains adhere to surface lattice sites via pair wise non-specific interactions. This simulation is aimed at single particle adsorption and multiple particle behavior to find the highest energy locations for given test surfaces and elucidate test surface that reduce adhesion energy. Parameters in this study are set by the particle, the surface and an interaction parameter between the two. Particle parameters include core diameter ($D$), grafting density of polymer ($\sigma$) and length of grafted polymer ($N$). Surface parameters include wavelength ($\lambda$) and amplitude ($A$). Our results show that the wavelength of surface features plays a significant role in the settlement of single particle systems and multiple particle systems. At $\lambda = D/2$ we observe a minimum in the adhesion energy and at $\lambda = D$ we observe a uniform settlement location of the particles. Increasing $N$ leads to a reduction in the effectiveness of surface topography to direct the settlement of individual particles into specific sites on the substrate.
Supramolecular strategies for the control of size and functionalization of organic and metal-organic framework nanoparticles

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Supramolecular chemistry promises the assembly of molecular units into well-defined architectures, via specific non-covalent interactions. Nanoparticles (NPs) possess unique size-dependent properties that are not observable in bulk materials. The combination of both fields is attractive, since stable, yet reversible hybrid assemblies hold great promise for biomedical applications.

Supramolecular nanoparticles (SNPs) are particles in which multiple copies of different building blocks are brought together by specific noncovalent interactions, resulting in assemblies that are typically larger than the building blocks themselves. NP formation based on supramolecular cyclodextrin host-guest interactions has been demonstrated by the groups of Davis [1] and Tseng [2] whereby the size of the formed NPs could be altered by varying the ratio of the monovalent and multivalent guest derivatives. These materials have been used for siRNA delivery and as MRI contrast agents, respectively.
Similarly, we have used cucurbit[8]uril ternary complexes in a similar manner to achieve size-controlled nanoparticles.[3,4]

At first sight completely unrelated is the area of metal-organic framework (MOF) particles. Also these are actively pursued for biomedical applications. At the same time, these are also constituted of small, multivalent building blocks. The same principle of capping with monovalent ligands has been used by us to achieve size control as well as functionalization in MOF NPs.[5]

In the current paper, we will discuss the physicochemical design rules of how the stoichiometry of the building blocks provides size control in both these organic SNPs as well as the MOF NPs. PEG chains of different MWs are attached to both types of particles and their effect on size control are discussed as well.

References


**COLL 476**

**Construction and drug delivery of supramolecular nanoparticles based on water-soluble macrocycles**

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Nowadays nanoparticles have obtained more attention based on their potential applications in drug delivery, sensing, imaging and chemotherapy. Among the broad diversity of supramolecular species as building blocks of nanoparticles, water-soluble macrocycles, such as cyclodextrins and sulfonatocalixarenes, are widely studied owing to their desirable advantages including efficient binding to drug molecules, biocompatibility and low cytotoxicity, convenient synthesis and easy size control, and robust stability under most in vivo conditions. In recent years, we construct a series of
cyclodextrin- and sulfonatocalixarene-based supramolecular nanoparticles as drug delivery systems and sufficiently investigated their biological functions with a special emphasis on their targeted delivery behaviors for different kinds of anticancer and Alzheimer's disease drugs including doxorubicin hydrochloride, paclitaxel, camptothecin, irinotecan hydrochloride, topotecan hydrochloride, and tacrine. The results show that the association of water-soluble macrocycles, drug molecules, and target units in a supramolecular assembly can improve the water solubility, increase the activity, and decrease the toxicity, of drug molecules, and the drug release can be smartly controlled through the assembly/disassembly of supramolecular nanoparticles responsive to multiple external stimuli, including temperature, host-guest inclusion, redox, and enzymatic catalysis.

We thank 973 Program (2011CB932502) and NNSFC (91227107) for financial support.

References


COLL 477

Out-of-equilibrium systems by dynamic and dissipative self-assembly
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The self-assembly of small molecules, polymers, proteins, nanoparticles and colloids under thermodynamic equilibrium conditions has been a powerful approach for the construction of a variety of structures of nano- to micrometer dimensions, like vesicles, capsules, and nanotubules. Despite these advances, the permanent nature of these synthetic self-assembled structures does not compare well to the complex spatiotemporally confined self-assembly processes seen in natural systems, which for instance allow the dynamic compartmentalization of incompatible processes, responsiveness, and self-healing. It remains a challenge to develop out-of-equilibrium systems through spatio- and temporal control over self-assembly.

In our research we focus on molecular approaches which allow control over self-assembly processes through covalent bond formation: (i) the development of dynamic covalent gelators, which allow spatial and temporal control over self-assembly by use of catalysts,[1,2] and (ii) dissipative self-assembly driven by a chemical fuel[3]. 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 of responsive, nanostructured and self-healing materials.


COLL 478

Specific DNA-mediated fusion of oil-in-water emulsions to detect biological markers

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A novel bio-sensing method was designed using DNA-mediated fusion of phospholipid and polyethylene glycol (PEG)-stabilized oil-in-water (O/W) emulsions. This method was inspired by the N-ethyl-maleimide-sensitive-factor attachment protein (SNARE) in cells,
which induces fusion between cell organelles and membranes. These bio-sensing droplets have cholesterol-anchored oligonucleotides incorporated in the shell, and the fusion of the droplets is driven by hybridization of these complimentary oligonucleotide strands in a zipper-like fashion. The droplet fusion was studied and optimized as a function of interfacial chemistry such as phospholipid chain-length (C18 and C22), PEG molecular weight and concentration, and orientation of oligonucleotides (zippering or tethering mechanism). Based on these studies, a thrombin sensor was designed using competitive binding of thrombin aptamer strands. One of the oligonucleotide strands was designed to partially hybridize to thrombin aptamer sequence, so that the thrombin aptamer had affinity for both thrombin and the oligonucleotide strands on the droplets. The droplet fusion increased as a function of thrombin in accordance with a simple binding model, with sensitivity down to 100 nM. Future efforts will focus on optimization of this sensing mechanism and new detection schemes for in-solution biochemical assays.

COLL 479

Surface properties of biological macromolecular nanoparticles revealed via their nanoscale hydrodynamics

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Surface properties of nanoscale supramolecular particulates play important roles to determine their assembly behavior and functionalities. Their direct evaluation often
evades the common structure examination techniques like x-ray/neutron diffraction and electron microscopy. Instead, they are often indirectly inferred or interpreted/rationalized based on the structure and property of the final products. In addition, the various non-covalent intermolecular interactions are intrinsically utilized in supramolecules design, synthesis, and assembly. Their surface properties are expected to be highly susceptible to solvation/suspension media environments, a fact that is employed as an effective mean to achieve the complex structures and adaptive properties of a supramolecular material. Therefore, for experimental attempts of effective evaluation of surface properties of supramolecular nanoparticles, the critical requirements should include, but not limited to, non-invasive (in-situ) nature of measurement techniques used. It is prohibited in many cases to use common scanning probe techniques like atomic force microscopy (AFM).

Laser light scattering serves as a viable tool for the purposes of in-situ experimental probe on supramolecular nanoparticles. The nanoscale hydrodynamics of particulates can be readily quantified with spectral broadening and shift of the light signal scattered from them, a form of Doppler Effect. In the present study, we demonstrate sensitivity and precision of the techniques using common proteins, the biological macromolecules inspire many synthesis efforts of supramolecules. Brownian motion and electrophoretic motion of protein molecules are directly evaluated in terms of their mean-square-displacement under thermal agitation and electrophoretic mobility under an electric field, respectively. From the measurement results, the surface characteristic of nanoparticles, such as surface area, surface charge density and electrostatic force/potential range (Debye length), can then calculated with Stokes-Einstein equation of translational friction force and Debye-Hückel-Henry theory of electrophoretic effect. Furthermore, it is shown that the effects of solvation/suspension media can be assessed well within the measurement certainty. The observation is discussed in the context of the well-established electrostatic double layer (EDL) theory.

COLL 480

Synthesis, self-assembly, and properties of organic supramolecular nanoparticles

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We will discuss the synthesis, self-assembly, and properties of capsular, supramolecular nano-particles. These are mono-dispersed, cavitand-based, assemblies with well-defined exterior shells defining internal volumes as large as 3200 Å³. Capable of encapsulating guests totaling seventy-eight (non-hydrogen) atoms, we observe a variety of packing-motifs within the inner space. We will discuss these, as well as our early observations as to whether or not homo- or hetero-guest pairing occurs when these complexes form. Understanding the rules governing how a guest or guests fill the inner space of these assemblies will provide important information regarding the long-term development of nano-reactors.
Development of supramolecular nanogating on mesoporous silica for in vivo therapeutic applications

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Although there have been improvements in cancer therapy over the past 50 years, the most effective methods for treatment today lie in early detection, broad spectrum chemotherapeutics and radiation therapies. Despite the fact that these treatments have drastically increased the survival rates of patients, they come at a considerable cost to the general health of the person receiving the treatment. Additionally, patients may not have continuous access to medical technology, resulting in advance stage cancers being detected where treatment options are limited.

To address these issues, my research group is taking a multidisciplinary approach to the chemotherapeutic treatment of cancer using mesoporous silica nanoparticles (MSNPs) gated by supramolecular nanosystems. MSNPs provide a unique platform technology in that they are modular. This approach allows for hyper-specific control of each of the nanoparticle functions, ranging from drug loading optimization to cellular targeting. Supramolecular valves, for example, allow for a range of adaptable
nanoparticle behaviors from simple, quick and reliable pore regulation to complex, multifunctional assemblies able to cater to many aspects of drug delivery.

My current research program is directed towards taking supramolecular nano-gates MSNPs from \textit{in vitro} development to \textit{in vivo} applications. My presentation will highlight some of our most recent efforts to fast forward MSNP drug delivery technology. Our investigations have led to experimentation with a novel drug design, adaptive surface functionalizations and integrated cellular targeting systems in effort to move our research towards a clinically viable alternative to current chemotherapeutics.

**COLL 482**

**Single atom alloys as a strategy for selective heterogeneous hydrogenations**

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Hydrogenation reactions are central to the petrochemical, fine chemical, pharmaceutical, and food industries and are of increasing interest in energy production and storage technologies. Typical heterogeneous catalysts often involve noble metals and alloys based on platinum, palladium, rhodium and ruthenium. While these metals are active at modest temperature and pressure, they are not always completely selective and are expensive. We have demonstrated that single palladium atoms can convert the otherwise catalytically inert surface of an inexpensive metal into an ultraselective catalyst. We used high resolution imaging to characterize the active sites and temperature programmed reaction spectroscopy to probe the chemistry. The mechanism involves facile dissociation of molecular hydrogen at individual palladium atoms followed by spillover onto the copper surface, where ultraselective catalysis occurs by virtue of weak binding. The reaction selectivity is in fact much higher than that measured on palladium alone, illustrating the unique synergy of the system.

**COLL 483**

**Hydrogenation of atomic nitrogen on the Pt(111) and Ru(0001) surfaces**

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The reactivity of nitrogen atoms on transition metal surfaces is relevant to a variety of catalytic processes. On Ru surfaces, the hydrogenation of N to form NH is the first step in the catalytic synthesis of ammonia, whereas N atoms are intermediates in NO reduction and in HCN synthesis over Pt catalysts. On Pt(111), a well-ordered p-(2×2)-N structure is formed from the reaction of ammonia with molecular oxygen, while on Ru(0001) p-(2×2)-N is formed from the dissociative adsorption of ammonia at 475 K. On both Pt(111) and Ru(0001), the hydrogenation kinetics of the p-(2×2)-N structures to form NH have been measured with reflection absorption infrared spectroscopy (RAIRS).
by following the growth of the NH stretch in the wavenumber range of 3310 to 3322 cm\(^{-1}\) as a function of time. In the case of Pt(111), the kinetics were measured in the temperature range of 180 to 200 K following the dissociative adsorption of H\(_2\)(g) on the surface at 85 K. As the activation barrier for NH formation on Ru(0001) is higher, the NH formation reaction was studied in the temperature range of 320 to 390 K in the presence of a background of H\(_2\)(g) at a pressure of 5×10\(^{-8}\) torr. On both surfaces, activation barriers for NH formation were obtained from Arrhenius plots and compared to theoretical values. On the Ru(0001) surface, a quantitative comparison of the kinetics of NH and ND formation indicate that quantum mechanical tunneling significantly affects the reaction rate, in agreement with previously published theoretical calculations. On Pt(111), atomically resolved images of the NH formation reaction have also been obtained with low temperature scanning tunneling microscopy. These images provide new insights into the RAIRS results, which showed multiple NH stretch peaks indicating a heterogeneous environment in the two-dimensional distribution of the NH molecules on the Pt(111) surface.

**COLL 484**

**Enantiospecific explosion of aspartic and tartaric acid on chiral Cu(\(hkl\))\(^{\text{R&S}}\) surfaces**

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Autocatalytic reaction mechanisms are observed in a range of important chemical processes including catalysis, radical-mediated explosions, and biosynthesis. Because of their complexity, the microscopic details of autocatalytic reaction mechanisms have been difficult to study on surfaces and heterogeneous catalysts. Autocatalytic decomposition reactions of tartaric acid (TA) and aspartic acid (Asp) adsorbed on Cu(110) offer molecular-level insight into aspects of these processes, which until now, were largely a matter of speculation. The decomposition of TA/Cu(110) is initiated by a slow, irreversible process that forms vacancies in the adsorbed TA layer, followed by a vacancy-mediated, explosive decomposition process that yields CO\(_2\) and small hydrocarbon products. Initiation of the explosive decomposition of TA/Cu(110) has been studied by measurement of the reaction kinetics, time-resolved low energy electron diffraction (LEED), and time-resolved scanning tunneling microscopy (STM). Initiation results in a decrease in the local coverage of TA and a concomitant increase in the areal vacancy concentration. On naturally chiral Cu(\(hkl\))\(^{\text{R&S}}\) surfaces, the autocatalytic explosive decomposition of both TA and Asp leads to extremely high enantiospecificity; enantiospecific rates that differ by two orders of magnitude. In the case of Asp it is possible to follow the enantiospecificity in mixed layers of D- and L-Asp in which the L-asp is isotopically labelled with \(^{13}\)C and thus, enantiodifferentiable from the D-Asp on the basis of its fragmentation pattern in a mass spectrometer.

**COLL 485**
Vinyl acetate formation pathways and selectivity on model metal and alloy catalyst surfaces

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Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium- and palladium-gold alloy catalyzed synthesis of vinyl acetate monomer (VAM). It is shown that vinyl acetate is formed on a Pd(111) model catalyst via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by β-hydride elimination to form VAM. The way in which adsorbate coverage affects both reactivity and selectivity is discussed. Gold-palladium alloys are found to improve the selectivity of the commercial catalyst. The origins of the catalytic selectivity and activity of the alloys are also investigated by exploring reactions on well-characterized Au/Pd(111) and Au/Pd(100) model alloys.

COLL 486

In-situ studies of the reactivity of copper surfaces protected by self-assembled monolayers

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In these studies two ultrasensitive techniques towards surface reactions, vibrational sum frequency spectroscopy (VSFS) and quartz crystal microbalance (QCM) have been integrated for in-situ studies of the corrosion of metal surfaces. This novel combination allows spectroscopic (VSFS) and mass (QCM) information to be acquired simultaneously with a high precision.

These studies have focused on reactions occurring on copper surfaces. This metal has numerous industrial applications, but suffers from corrosion in several environments. Thus, in order to avoid degradation of the metal, effective protective films are necessary. The use of self-assembled monolayers (SAMs) of alkyl thiols to protect copper surfaces has advantages such as that objects of any shape can be coated (e.g. microelectronics where traditional coatings are too thick), and that the thickness of the film can be controlled on the Ångström level by changing the chain length.

The VSFS/QCM setup was used to study the oxidation of copper surfaces covered by a monolayer of octadecylthiol exposed to dry air. By monitoring changes in the non-resonant background in the sum frequency spectra due to the formation of Cu2O, VSFS (as well as QCM) allowed the detection of less than 5% of a monolayer of the oxidation
product. An almost perfect correlation was found between the changes in the non-resonant background in the VSF spectra and the mass changes observed by QCM. Further, infrared reflection/absorption spectroscopy (IRAS) was used in-situ in combination with VSFS to examine the protective ability of SAMs of alkyl thiols of different chain lengths, as well as alkyl selenols adsorbed on copper surfaces. Upon exposure to humid air containing sub-ppm levels of formic acid, IRAS provided information about the nature and the kinetics of formation of the reaction products. As a complement, VSFS provided detailed information about changes in the molecular structure of the SAMs.

**COLL 487**

**Nucleation and growth of ice films on metal surfaces**

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We employed Scanning Tunneling Microscopy (STM) to access the morphology of ice films as many as 30 molecular layers thick; for thicker films AFM has to be used. The observed morphology yields new insights about water-substrate interactions and how they affect the structure of ice films. This talk gives an overview of this progress for crystalline ice films on Pt(111). STM reveals a first molecular water layer very different from bulk ice: besides the usual hexagons it also contains pentagons and heptagons. Slightly thicker films (∼1nm, at T>120K) are comprised of ∼3nm-high crystallites, surrounded by the one-molecule-thick wetting layer. These crystals dewet by nucleating layers on their top facets, at a rate determined by the crystal height and the energy of the ice-Pt interface. For T>115K surface diffusion is fast enough that surface smoothing and 2D-island ripening is observable. By quantifying the T-dependent ripening of island arrays we determined the activation energy for surface self-diffusion. The shape of these 2D islands varies with film thickness. We attribute this to a transition from polarized ice at the substrate towards proton disorder at larger film thicknesses. Despite fast surface diffusion ice multilayers are often far from equilibrium. For example, the crystal structure of ice, deposited at ∼140 K, switches twice as films grow thicker. Isolated 3D clusters, which can only grow via layer nucleation, consist of hexagonal ice. Following coalescence, cubic ice is being produced in growth spirals created above substrate steps. Eventually, at thicknesses of ∼20 nm, double growth spirals become dominant generating hexagonal ice.

*Joint work with N.C. Bartelt and S. Nie, Sandia Natl. Labs, CA., supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. DOE under Contracts No. DEAC04-94AL85000, and by the Laboratory Directed Research and Development program at Sandia National Laboratories.*

**COLL 488**

**Structure-function studies using plant virus-based cargo-delivery systems**
Structure-function studies using plant virus-based cargo-delivery systems

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A quintessential key in nanotechnology is to self-assemble multifunctional nanoparticles with well-defined properties. The in vivo fate, i.e. cellular uptake, biodistribution and clearance, of nanomaterials is dependent on their physiochemical properties such as shape, size, and surface chemistry. For nanomedical applications, precise formulation of homogeneous and monodispersed materials in thus an important goal. Nature has already perfected the self-assembly of various nanostructured molecules and materials; therefore we have turned toward the structures of plant viruses (termed viral nanoparticles, VNPs). These highly symmetrical macromolecular assemblies come in various shapes and sizes, but each species is highly monodisperse. VNPs have a high degree of symmetry and polyvancy. They consist of hundreds of copies of identical coat proteins, therefore VNPs have properties of polymeric macromolecules. 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. VNPs are highly dynamic structures, that can be dis- and re-assembled around artificial cargos, shapes can be switched (sphere-to-rod, and rod-to-sphere). Furthermore, the aspect ratio of rod-shaped VNPs can be tightly controlled through genetically-templated self-assembly.

In this presentation, we will highlight structure-function studies specifically characterizing biodistribution and tissue-specificity of VNPs of varying geometries, i.e. size, flexibility, aspect ratio. We will highlight novel chemical synthesis protocols that allow shape switching of VNPs, facilitate the synthesis of rods of varying but defined aspect ratios, and self-assembly of co-operative VNP networks and chains. We will discuss preclinical research on the application of VNPs in molecular imaging and drug delivery.

COLL 489

Tobacco mosaic virus as a powerful anisotropic building block to modulate cellular responses

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Our recently data have demonstrated that some plant viral particles (including tobacco mosaic virus, TMV) can significantly accelerate the osteogenesis of bone marrow stromal cells without supplementing any exogenous protein or drug. In addition, the surface functionalization of viral particles can further augment such cellular response. Here we report that the combination of the surface modification of TMV with controlled 3D assembly of TMV particles can serve as programmable building blocks to modulate cellular responses. Our approach took advantage of the unique structural features of TMV. It may lead to novel tissue engineering materials which can simultaneously fulfill the hierarchical structural, mechanical and biochemical requirements.

COLL 490

On the influence of surface chemistry and 3D microstructures on the shape of the cell nucleus

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The use of artificial materials in medical applications requires a detailed understanding and control of the adhesion of cells to synthetic surfaces. Three main factors influence the interaction of cells and cell organelles with surfaces: topography, surface chemistry and mechanical properties of the substrate, as they all play a role in the interaction between surface, extracellular matrix and cell membrane. An interesting case of the behavior of cells on surfaces is the behavior of osteosarcoma cells (SaOs-2) on microstructured substrates. These bone cancer cells exhibit a strong deformation of the cell nucleus when brought into contact with micro-structured surfaces¹.

In our contribution we systematically study the influence of the surface chemistry and shape of specifically designed micro-structured, polymer-coated surfaces on the adhesion and morphology of cells and their nuclei, which had been seeded onto these substrates. (Figure 1A-D). We generate large arrays of micropillared surfaces with variation of the size, height and distance of the pillars. In addition, we design the surfaces such that either the whole surface or only the top of the pillars or only the space between the pillars are made cell repellent and compare to situations where the whole microstructure is made cell adhesive.
REFERENCES


COLL 491

Morphology control of TNTZ alloy using hydrothermal process for apatite induction

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A new B phase Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy was developed for biomedical materials by Niinomi et al. It does not contain any toxic elements and has some excellent features such as mechanical properties, better cyto-compatibility and higher corrosion resistance. Since TNTZ alloy surface is bioinert, their surface was hydrothermally treated to attain bioactive sodium titanate layer on it. Sample was treated in 5M NaOH solution containing 0.2 w% NH₄F as an additive at 90 and 150°C
for 2 hours. Surface treated at 90°C had a relatively flat mesh structure as shown in Fig. 1(a). On the other hand, surface treated at 150°C had a rough mesh structure shown in Fig. 1(b). That was because titanium was easily dissolved in the solution and thicker sodium titanate layer was formed at higher temperature. After hydrothermal treatment, samples were soaked in SBF solution for 2 weeks to induce apatite on the sodium titanate layer. Though both samples (a) and (b) in Fig. 1 showed a bioactivity, sample (a) did not induce apatite densely but sparsely as compared in Fig. 1(c) and (d). From this result, it was assumed that sample (b) having rougher surface could accelerate the apatite induction.

Fig. 1 (a) 90°C before SBF soaking, (b) 150°C before SBF soaking, (c) 90°C after SBF soaking, (d) 150°C after SBF soaking


COLL 492

Novel mimetic cell membranes: From in vitro towards in vivo applications

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In nature, cell behavior is guided by complex physiochemical cues encoded in their environment. For example, a wealth of stimuli ranging from cell-cell contacts, cytokine and growth factor stimulation, ECM interaction and the physical milieu have been identified to steer (stem) cell fate. Here, the cell plasma membrane plays a pivotal role, providing a physical barrier to the cells surroundings and allowing transport and signal transduction. This highly ordered and complex interfacial lipid layer can house a fast array of bio-active compounds and is heavily involved in cell migration, proliferation and differentiation. Reconstituting its function is crucial to further our understanding of such cellular processes. Mimetic membrane systems, in the form of Supported Lipid Bilayers (SLBs), have been put forth to explore the cell membrane in a redundant fashion. A key feature of SLBs is the fluidic nature of the lipid bilayer and embedded components.

In the present work, a novel nano-analytical device facilitated separation of membrane components using µSLB electrophoresis. In addition, µSLB electrophoresis was used to generate reversible locked-in SLB gradients amendable to a variety of (bio)chemistries. Moreover, a propitiatory biopolymer surface modification strategy allowed us to prepare air-stable Biomaterial Supported Lipid Bilayer (BSLBs) that retain their non-fouling behavior and fluidity in 3D. Mesenchymal Stem Cell (MSC) culture with RGD peptide amphiphiles was studied, suggesting chemical, mechanical and biological decoupling of bulk material properties.
Bright fluorescence imaging of cells cultured on the plasmonic dish

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A plasmonic chip, a periodic structure coated with thin metal films, has been applied to bio-imaging¹ and bio-sensing. An enhanced electric field based on the grating-coupled surface plasmon resonance provides the enhanced fluorescence from fluorescence molecules on the plasmonic chip. In this study, a two-dimensional plasmonic dish was fabricated as the cell cultivation dish by changing the bottom plate of glass-bottomed dish from a cover glass to the plasmonic chip, and cells cultured were observed with fluorescence microscope.

A plasmonic dish was produced by the following two ways: 1) uv-nanoimprint lithography using a UV-curable resin (TOYO GOSEI, PAK02-A) and 2) integrally molded method (Seikoh Giken). The pitch and hole depth of replica were 500nm and 30nm. The coating layer were silver, SiO₂, and Ti layers. Primary hippocamal nerve cells or Human Embryonic kidney (HEK) cells were separated on these dishes. They were kept in an incubator maintained at 37 °C. For nerve cells, immunostaining was performed with MAP2 and Alexa-labeled antibody. As for HEK cells, membrane protein with SNAP-tag was designed to be exposed out of cells and modified with Alexa-labeled antibodies. Cells were observed under the fluorescence microscope equipped with halogen and Hg lamps, an electron multiplying charge coupled device (EM-CCD) camera (Luca-r, Andor).

The fluorescence images of nerve cells on the conventional glass-bottom dish and on the plasmonic dish were observed with upright fluorescence microscope. The fluorescence image on the plasmonic dish was 10 times brighter than that on the glass-bottom dish. In HEK cell observation, the 10 times fluorescence enhancement was also obtained. Cells cultured on the plasmonic dish showed the advantage for providing brighter and surface-selective fluorescence image with a high space resolution under the conventional microscope.

Developing an artificial adult stem cell niche would provide a valuable tool for treating various diseases. The dental epithelial stem cell (DESC) population present in the cervical loop of continuously growing rodent incisors provides an informative model system to study adult epithelial stem cells. This has applications not only for enamel regeneration, but also possibly for any epithelial tissue containing adult epithelial stem cells. Despite much progress in understanding the epithelial/mesenchymal crosstalk in this DESC niche in the incisor cervical loop, there is little known about the role of the physical microenvironment and topography on the maintenance of these stem cells. To better understand the contribution of topography to DESC maintenance and differentiation, DESCs were isolated and characterized from the labial cervical loop of the mouse mandibular incisor. Our results revealed E-cadherin and Integrin alpha-6 as potential markers of dental epithelial stem cells, and we found differential localization of extracellular matrix proteins within the cervical loop microenvironment. To understand the physical topography and architecture the DESC experience, we performed 3D reconstruction analysis of histological sections to determine the size and volume of the mouse cervical loop. To study the effects of microenvironment on the self-renewal and differentiation of murine DESCs, we fabricated a series of polydimethylsiloxane (PDMS), polycaprolactone (PCL), and polystyrene (PS) scaffolds, modeled from the 3D reconstruction, containing varying micro- and nano- topographies using standard photolithographic techniques. Insights into the effects of topography on stem cell maintenance and differentiation could prove beneficial for the successful regeneration of bioengineered teeth from adult stem cell populations and would advance the treatment of both congenital disorders and tissue damage from trauma and disease.

COLL 495

Synthesis of artificial cilia

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One of the rapidly growing fields in biotechnology is the use of lab-on-a-chip devices to analyze biofluids. A typical lab-on-a-chip system would consist of a number of microfluidic channels connecting microchambers where dedicated biochemical analysis is carried out. For microfluidic fluid transport, structures that could create flow in microchannels need to be designed and artificially controlled cilia fulfill those expectation. Cilia are tiny hair-like appendages (with a typical length of 10 µm and a diameter of 250-500 nm) that cover for example the surface of many micro-organisms which helps them move and also the inner layer of mammalian trachea, where they help in expelling mucus from the lungs. Most examples of artificial cilia in literature are
controlled by external forces such as magnetic, electric, pH gradients or piezo-actuation forces. Here we demonstrate a way to design flexible cilia-like structures which are comparable in lengths to biological cilia and which are driven by internal chemical stimuli. These cilia-like structures are fabricated out of flexible polymers like PDMS or polypyrrole and have a metal cap. In the presence of appropriate substrate, the metal cap undergoes a reversible reaction and induces an oscillatory motion in the rod.

**COLL 496**

**Microfibrous films reduce fibrotic encapsulation through the TGFβ pathway**

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Fibroblasts play a critical role in normal wound healing, but this process can be unintentionally activated upon implantation of medical devices. This activation can result in fibrotic encapsulation and lead to device failure. Within fibrotic tissue, fibroblasts undergo myofibroblastic differentiation, initiated by TGFβ signaling. This differentiation is culminating in the expression of α-smooth muscle actin (αSMA) and increased production of extracellular matrix (ECM) components, such as collagen I and III. Our previously published results demonstrate that topographic cues down regulate both TGFβ signaling and myofibroblastic differentiation in fibroblasts. Yet, it is currently unclear the mechanism through which topography regulates myofibroblastic differentiation and fibrosis.

We have fabricated a series of films with micro-sized fibers by laminating medical grade polypropylene through a microporous polycarbonate membrane. The fiber length and diameter can be reliably controlled allowing tunable topography. As fiber length increases, the characteristic elongated morphology of cultured fibroblasts decreases dramatically. Intercellular tension is also decreased, as marked by a decrease in phosphorylated myosin light chain. Moreover, as fiber length increases, fibroblastic gene expression for components of the TGFβ pathway, including TGFβ1, Smad3 and TGFβ receptor II (TβRII) decreases. This reduction suggests that fibroblasts become insensitive to TGFβ as fiber length increases. As expected, the reduction in TGFβ signaling results in a decrease in αSMA, Colα2, and Col3α1 gene expression. In an in vivo wounding model, microfiber films implanted in the subcutaneous layer of wild type mice dramatically reduce deposition of collagen around the films compared to flat controls. This result suggests that modifying the surface of a material to include microfibers could reduce fibrotic encapsulation of implanted medical devices. The mechanisms elucidated by further studies could also reveal novel therapeutic targets for fibrotic diseases such as keloids and hypertrophic scars.
Improving human well-being on a resource-limited planet - can we do it?

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As the demands of the global - and rapidly growing - middle-class spiral upwards, the challenges to our planet of climate change and ocean degradation dominate. But we also face the challenges of maintaining sustainable food, mineral, freshwater and energy supplies at an economically affordable cost. These 21st century challenges are qualitatively different from those we overcame so successfully in the 20th century, when well-being - health, life expectancy and quality of life - took a leap forward for many humans, especially in the so-called developed countries. What we need now is a renaissance in our thinking, a re-evaluation, so that we place human well-being alongside ecosystem and resource management, in order to plan an equitable and sustainable future for all, including those who have been excluded from betterment until now. The challenges demand innovation, seizing new opportunities for science and technology to work alongside the humanities and social sciences. Policymakers, the private sector, and the public sector will all have to embrace the changes. Coordination and collaboration offer the only prospect of success. There are exemplar nations beginning to develop the way forward, but national and global governance require investment and strengthening. Time is not on our side.

Sunpower: Setting a global challenge

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In two recent and timely contributions, Dave King and Richard Layard have argued persuasively that to tackle the world's burgeoning problem of climate change, inexhaustible solar power – Sunpower – must be rapidly advanced to the forefront of global research, development and implementation of non-carbon energy sources (1). It is universally recognised that Sunpower is the only renewable resource available to humankind that has enough terrestrial energy potential to satisfy – actually, to exceed – our necessary present and future carbon-free energy (2,3). No other sustainable energy source comes close.

However, capturing, converting and ultimately delivering and distributing the sun's power poses formidable challenges from scientific, technological, socio-economic and socio-political perspectives. Notwithstanding, King and Layard note that these are just the sort of coupled, multidisciplinary and – above all else – breathtaking high-level challenges for Sunpower that can only be solved through engaging the best minds in a major international collaboration.
Such a global Sunpower initiative will provide the natural, multidisciplinary focus for a major international strategy to bring the full power of our science and intellect to deliver real energy solutions. I will present a personal perspective on the scientific challenges and innovations necessary for a global energy system based on Sunpower as input, and electricity and chemical fuels as outputs. This will help guide strategies to the Sunpower challenge – a challenge truly global in character, implementation and impact.


The support of the King Abdulaziz City for Science and Technology-Oxford Petrochemical Research Centre (KOPRC) is greatly appreciated.

COLL 499

Powering the future with thin-film printed solar cells

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Solar energy is set to make an increasing contribution to global energy needs into the future. While traditional Si-based solar cells are well known, they are expensive to manufacture in terms of both energy and infrastructure. The CSIRO, Australia’s government research agency, has been working with university and industry partners under the Victorian Organic Solar Cell Consortium (VICOSC) to develop the capability to print thin-film solar cells onto plastic. This technology offers several distinct advantages over traditional solar cells. In particular, thin-film printed solar cells are lightweight, flexible, semi-transparent and inexpensive to manufacture. This makes them well suited to a much wider range of applications than traditional Si, including integration into product packaging, servicing the energy needs of remote communities, and incorporation into the windows of skyscrapers. The VICOSC consortium has become a world leader in the area of large-scale solar cell printing and is now well positioned to translate this work into products. Our public engagement activities will also be discussed.

COLL 500

Putting science into foreign policy

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The speaker will describe his recent role as the first Chief Scientific Adviser to the UK Foreign and Commonwealth Office. He will describe a range of projects he was involved with including Antarctic science, research in the pristine waters of the British Indian Ocean Territory, emergencies such as Fukushima, issues involving chemical and biological weapons and the promotion of science in the Middle East [1]. The challenge of undertaking new international science projects in the framework of complicated political environments will be emphasised.


COLL 501

Facing the challenges of the "Middles"

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The world has quietly entered a new age characterized by the fast rise of large number of middle class, the rapid growth of middle-income countries, especially the emerging economies, and the concern of middle-income traps. All three middle's are interconnected in some perplex ways, posing serious challenges to the emerging economies, and indeed, to the world as a whole. To a large degree, the future of the world rely on how the challenges of these middle's are dealt with.

Professor Sir David King has been a leading voice and thinker on the issues related to the rapid growth of the world middle class. Unlike the conventional perspective that treats the food, energy and water (FEW) problem as a problem of population growth, he sees the problem from the perspective of the growth of middle class in the world. In fact, most of world's environmental and resource problems seem to be related, one way or the other, to the growth of middle class. While a greater population of world enjoys the benefit of modernization, human beings for the first time is severely constrained by the limits of the resources and by the planetary boundaries. This paper will present a synthesis of the related thoughts and studies, and will try to put together the three middle's into a synthetic framework. It will take the case of emerging economies for analysis and demonstration.

The paper is inspired by the work and teaching of Professor Sir David King to whom it is dedicated.

COLL 502

Climate science and future climate governance

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The international governance of climate change is about to enter a new era. To create an effective regime, much innovation will be required. In particular, there is a need to reconcile the bottom-up policy-based actions available to governments with the increasingly stark scientific picture of the science of climate change. The design of a post-2020 climate agreement will need to avoid the chronic weaknesses that undermined the Kyoto Protocol, but will also have to grapple with the emergence of inevitable tensions between different parts of the developing world.

COLL 503

Designing biomimetic capsules and gels that undergo directed movement

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Social insects and amoebas undergo auto-chemotaxis: they move in response to self-generated chemical gradients. Using computational modeling, we design polymeric microcapsules and gels that mimic salient features of this biological behavior. Namely, these polymeric materials can generate chemical gradients, sense the self-generated gradients and then autonomously move in response to these gradients. This behavior allows the microcapsules to self-organize into various self-propelled structures and even exhibit ant-like tracking behavior. The gels also spontaneously self-aggregate into larger clusters, resembling the auto-chemotactic behavior of amoebas. Both examples reveal how biomimetic, chemo-responsive systems can display complex, cooperative behavior. Notably, these systems can have important technological applications. In particular, we show how the microcapsules can be used to selectively pickup and deliver cargo in microfluidic devices. We also show how that the self-propelled gels autonomously communicate with each other to recombine into a single unit after the material was cut into separate pieces, and thus, these gels constitute novel self-healing materials.

COLL 504

From Langmuir monolayers to layer-by-layer assembly

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Much has been learnt in the past 3 decades about Langmuir Monolayers due to the introduction of new techniques, namely optical microscopy and surface X-Ray diffraction, later FTIR spectroscopy. This led to the notion of a richness of phases as well as to peculiar domain structures due to long-range electrostatic forces arising at interfaces. Extending these studies to more complex films of biological molecules this could contribute much to the understanding of processes at membrane surfaces. However, it also demonstrated that films built up from these monolayers have a complex domain structure and in case of “perfect” organization do not dissolve functional molecules. Functional organized films therefore require alternatives to the
Langmuir-Blodgett technique, and one of the most promising is “Layer-by-Layer-Assembly”. With this technique one adsorbs alternatingly molecules, ions or particles of opposite charge, and this leads to multilayers of defined thickness and roughness with precision of nm. The structure is well characterized by X-Ray-, Neutron and light reflectivity, the permeation by optical spectroscopy. Due to the high modularity and versatility of the process multifunctional films can be build up, promising many applications in Bio- and materials sciences. As the technique relies on adsorption also curved and porous solids can be coated, and one thus obtains functional colloids. Selecting sacrificial cores one further obtains micro- and nanocapsules with well-defined walls. Controlling the intermolecular interactions inside these walls one can control their permeability and mechanical properties. This has been achieved via changes of pH, temperature, salt, electrochemical potential or chemical reactions as well as via external light, microwaves or acoustic fields, as will be demonstrated by optical and force spectroscopic studies. The processes are at least qualitatively understood and quantitatively controlled, so that they now invite many different applications. Examples on this to be presented vary from light triggered intracellular release of a signal peptide to follow an immune reaction to release of anticorrosion agents to fabricate a self-repairsing coating.

**COLL 505**

Nano Letters Young Investigator Award Lecture

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The core of our research program is materials innovation for enabling new device structures and concepts. We study a wide range of electronic materials in both planar and 3D geometries. In all cases, we explore new schemes of manipulating, processing, and engineering materials - often at unprecedented levels - to enable new functionalities and properties.

**COLL 506**

Molecular-scale hydrophobic interactions between hard-sphere reference solutes are attractive and endothermic

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The osmotic second virial coefficients, B₂, for atomic-sized hard spheres in water are attractive (B₂ < 0) and become more attractive with increasing temperature (∆B₂/∆T < 0) in the temperature range 300 K ≤ T ≤ 360 K. Thus, these hydrophobic interactions are attractive and endothermic at moderate temperatures. Hydrophobic interactions
between atomic-sized hard spheres in water are more attractive than predicted by the available statistical mechanical theory. These results constitute an initial step toward detailed molecular theory of additional intermolecular interaction features, specifically, attractive interactions associated with hydrophobic solutes.

**COLL 507**

**Surface tension as opposed to hydrophobicity**

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We discuss recent experiments and theories concerning protein collapse and folding in aqueous solvents. Experiments using multicomponent solutions have revealed much about the mechanism of folding. Simulation and theory have been used to interpret thermodynamic and fluorescence correlation spectroscopy experimental results. We will discuss recent simulation results which impact folding theories. New measures of protein stability tendencies offer a different view than the poorly defined hydrophobic effect. We choose to look at glycine rich systems which are intrinsically disordered and alanine systems which have more hydrophobic surface area than glycine. We conclude that surface tension derived from the van der Waals potential interactions with water does not drive protein collapse.

**COLL 508**

**Hydrophobic and electrostatic interactions at aqueous interfaces: Implications on assembly**

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Structure, dynamics, and density fluctuations of water are significantly different near extended hydrophobic interfaces, which influence water-mediated interactions between hydrophobic or between ionic solutes near interfaces. I will present results from extensive molecular dynamics simulations that show that hydrophobic interactions are qualitatively different near air-water interface of water, leading to weaker driving forces, and faster kinetics of assembly. In contrast, electrostatic interactions are significantly enhanced near an air-water interface, resulting from the balance of water structure, capillary fluctuations, and interface deformation. Together these results imply a qualitatively different nature of self-assembly in interfacial environments relative to that in bulk.

**COLL 509**

**Role of water in protofilament assembly and amyloid polymorphism**
I will discuss the role of water in protofilament formation from peptides from Aβ and yeast prions. In addition, the potential role of water in determining polymorphism in amyloid fibrils will be discussed.

COLL 510

Hydration and hydrophobic effects on helix formation of polypeptide chains in open nanotubes

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We describe all- atom molecular dynamics simulations of a polypeptide in open nanotubes to elucidate the effects of confinement, hydration and hydrophobic interactions on helix formation. A phase diagram is constructed and the role of water in helix formation is discussed.

COLL 511

Electron transfer and carbon-carbon bond cleavage by cytochromes P450

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The mechanisms of cytochrome P450 catalyzed deformylation have been strongly debated and difficult to unravel. These reactions require three separate oxidation steps, culminating in an enigmatic deformylation and stereoselective desaturation of the substrate. Herein, the deformylation mechanism of the sterol 14α -demethylase (CYP51) as predicted by a multifaceted computational approach is described. These results provide strong theoretical support for operation of the peroxo intermediate in CYP catalyzed deformylation. Molecular dynamics simulations support that the lanosterol carboxaldehyde diverts the hydrogen-bonded network of water away from the peroxo (Fe3+O22-) and hydroperoxo (Fe3+O2H2-)species to attenuate protonation. In turn, hybrid quantum mechanics/molecular mechanics predict that the aldehyde is trapped by the peroxo intermediate as a tetrahedral peroxyhemiacetal. This defines a branchpoint for a concerted deformylation mechanism from which a stepwise mechanism initiated by cleavage of the C-C bond was found to be more energetically feasible. Population analyses of the peroxoformate/deformylated substrate complex indicate that heterolytic cleavage of the C-C bond in the enzyme environment generates a carbanion localized to
the steroid substrate. Conversely, in the absence of the protein electrostatic background, the C-C cleavage reaction proceeds homolytically, indicating that the active site environment exerts a strong modulatory effect on its electronic structure. After expulsion of the formic acid, Compound II readily abstracts the 15R-hydrogen, thereby inserting the 14,15 double bond into the steroid skeleton. Parallel studies considering addition of hydroxyperoxo to the aldehyde indicated that this reaction proceeds with high energetic barriers. Taken together with our other work on this enzyme family, we aspire to provide a unified mechanistic view consistent with decades of experiments and provide general mechanistic insight into the catalytic mechanisms of several cytochrome P450 enzymes. In effort to validate the theoretically derived mechanism experimentally, results describing matrix isolation and preliminary spectroscopic characterization of the oxyferrous, peroxo and hydroperoxo species in wild-type and site directed mutants of the Mycobacterium tuberculosis CYP51 will also be described.

**COLL 512**

**Some basic common sense statements about the interaction of colloidal nanoparticles with cells**

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Some common sense statements about the interaction of colloidal nanoparticles with cells are given. While detail of this interaction strongly depends on the precise properties of the nanoparticles, the type of cells, conditions of incubation, etc. still some basic universal common sense dependences exist, which will be outlined. In general small, elongated, positively charged, soft particles are incorporated in vitro by cells to a higher extend than big, flat, negatively charged, stiff particles.

**COLL 513**

**Molecular response as an indicator of the interaction at the interface of the engineered nanomaterial and the organism**

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**<h2>Assessing the Implications of Nanotechnology</h2>**

Engineered nanomaterials have tremendous potential to benefit the environment, but despite 10 years of research uncertainty remains about their environmental fate and effects of these materials, models to describe their behavior are still lacking. This
symposium will explore the need to understand nanomaterials life cycle, releases, exposure, fate, and effects in a comprehensive manner. Papers that provide mechanistic insights into how the nanomaterial properties lead to the observed efficacy of application, reactivity, or toxicity are highly desired. Papers presenting the development and validation of models for predicting nanomaterial release, fate or effects are also highly desired. Papers with these and related topics will be given highest priority for oral presentations.

COLL 514

Comparative study of functionalized gold nanoparticle toxicity on bacteria and Daphnia gene expression

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Nanoparticles are being applied to various fields due to their unique properties. However, with the anticipated increase in nanoparticle use, the risks of nanoparticle exposure to ecosystems need to be assessed. As the mechanism of toxicity remains largely unclear, untargeted, sensitive and fundamental studies evaluating biological response to nanomaterial exposure are needed. This research seeks to assess and compare the toxicity of functionalized gold nanoparticles on gene expression changes in Shewanella oneidensis MR-1, a beneficial bacteria species in the ecosystem, and Daphnia magna, a water flea used as a model organism in aquatic toxicology, aimed at understanding the fundamental molecular mechanism underlying nanotoxicity across different species.

COLL 515

Abiotic and biotic interactions of manufactured nanomaterials in the terrestrial environment

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Terrestrial environments provide important ecosystem services including nutrient cycling by microbes, food production, and, to a degree, waste treatment. Although soil matrices are heterogeneous and complex, the transformations underpinning ecosystem services occur by physical and chemical processes that may be catalyzed, biotically or
abiotically, at interfaces: air-water, solid-water, and solid-solid. Additives to soil are subject to, altered by, and can feed back to affect, the involved processes. Such additives include manufactured nanomaterials (MNMs), based on their manufacture, uses, and fates. Here, we discuss MNMs relative to interfaces in natural soil and the processes that occur there. What are MNM physicochemical characteristics within soil? How do MNM characteristics affect MNM bioavailability to soil microorganisms? How do MNM interactions with soil microorganisms, including exopolymeric substances surrounding microbes, affect MNM interactions and fates, in soil? We discuss these and related questions, drawing upon our work in the UC Center for Environmental Implications of Nanotechnology (UC CEIN) and upon the work of others studying MNM entry, transport, transformation, and effects in natural soils.

**COLL 516**

**Impacts of differing diamond and gold nanomaterial surface chemistries on toxicity to *Daphnia magna*: Defining trends in nanomaterial toxicity**

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The factors that determine the interaction of manufactured nanoparticles (NPs) with biological entities have yet to be fully defined. It will be critical to develop an understanding of these factors to develop materials that do not cause environmental harm and therefore are sustainable. Surface chemistry in particular may significantly influence NP toxicity by changing NP uptake, interaction with cells and toxicity or by carrying toxic ligands into the organism. In this study, the impacts of differentially functionalized gold and diamond NPs on mortality, reproduction, and body size in the toxicological model species, *Daphnia magna*, were compared over acute and chronic exposures. Acute assays show that negatively charged gold and diamond NPs are orders of magnitude less toxic than their positively charged counterparts. The results show that certain ligands used in NP functionalization can directly contribute to and increase toxicity of NPs. NPs may also increase the toxicity of ligands by potentially localizing the ligand concentration and exposure. In addition, similarly functionalized diamond and gold NPs differ in their impact on *D. magna*, which appears to be associated with particle stability. This research indicates NP toxicity is not solely due to surface charge but also may be dependent upon other properties such as ligand density, structure or particle aggregation. These results demonstrate that specific NP properties have great implications for determining NP toxicity and creating sustainable nanotechnologies may involve several aspects of NP design.
Direct and indirect toxic effects of engineered nanoparticles on microalgae: The role of natural organic matter

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In order to assess the overall risk posed by engineered nanoparticles (ENPs), the biological effects of this emergent pollutant to aquatic ecosystems must be evaluated. We present findings from studies conducted with a diversity of ENPs (metallic, quantum dots) on a variety of freshwater and marine microalgae (phytoplankton) illustrating both their direct and indirect effects. We show that in general, while the surface properties of ENPs govern their aggregation behavior and ionic strength and salinity controls their dissolution, exopolymeric substances (EPS) produced by algae influence their toxic and thereby movement through the water column and food web. The production of EPS reduces the impact of ENPs (bioavailability and toxicity) and/or their ions on cellular activities of microalgae. It does not however directly reduce the aggregation and/or solubility of ENPs but rather affects their stability. Complicating understanding of these interactions is the great assortment of surface coatings for ENPs. This perspective is intended to highlight our current knowledge and the need for future research particularly focused on determining the fate and transport of ENPs in the aquatic ecosystems.

Effects of engineered metal and metal oxide nanoparticles on model aquatic organisms: Finding protein targets by redox proteomics

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Biological systems interact with environmental chemicals in complex ways and biochemical markers (biomarkers) often provide informative information on both extent of toxicity and biochemical toxicity mechanisms. In aquatic toxicology, it is common to use bivalve species as sentinels in marine and estuarine contexts and Daphnia as a sentinel in freshwater. We have applied redox proteomics as a means of assessing environmental stress in aquatic environmental contexts for many years. Nanomaterials represent a novel category of environmental chemicals which pose unusual questions to the toxicologist. What is meant by dose? Are particles taken up by organisms and can we follow their fate in multi-organ organisms? What aspects of the nanomaterial's structure and chemistry impacts on toxicity? In particular, a key unanswered question is how does the context of nanoparticle exposure influence toxicity? In aquatic systems there is scope for particles to agglomerate, dissolve or otherwise interact with the aquatic or sediment surrounding them. This talk focuses on three experiments in our lab in which well-characterised, engineered metal or metal oxide nanoparticles were exposed to test organisms: 1) the bivalve Mytilus edulis; 2) the water-flea Daphnia magna and 3) cultured human astrocyte cells. Our approach is to expose to doses of nanoparticles and to identify redox proteomics targets which then yields insights to likely biochemical consequences of these nanoparticles. We have developed a toolkit of gel-based and gel-free approaches for identifying and enriching for proteins yielding insights in particular to their carbonylation or thiol oxidation. The proteome seems to adapt quite quickly and in a dose-related manner to challenge by certain metal oxide nanoparticles in terms either of change of protein abundance or change in protein oxidative status. These effects are also somewhat species-specific.


**COLL 519**

**Nanoparticle toxicity assessment in a bacterial model**
Engineered nanoparticles are found in many everyday products and hold great potential as therapeutic agents. Accordingly, it is critical to consider how engineered nanoparticles interact with physiological and ecological systems. This work focuses on functional assessment of bacterial cell response following exposure to Au, nanodiamond, and semiconductor nanoparticles. Functional considerations include biofilm formation, cell delivery of chemical messengers, production of reactive oxygen species, and gene expression, among others. In this new collaborative study, obtained bacterial toxicity results can be compared to those obtained in other model systems (lipid bilayers and the multicellular water flea, Daphnia) to identify common modes of nanoparticle interactions and the resultant effects. The goal of this work is to discover critical nanoparticle features that determine cellular toxicity and then redesign nanoparticles to promote sustainable use.

**COLL 520**

**Influence of substituents and functional groups on the surface composition of ionic liquids**

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Ionic liquids (ILs) are molten salts with a melting point below 100 °C. The enormous variety of cation-anion combinations enables tuning of the physico-chemical properties of ILs over a wide range. Functional groups can be implemented in their chemical structure to adapt them for specific tasks - such functionalized ILs are known as “task-specific ionic liquids”. They are used in a variety of applications, from catalysis and organic synthesis to extraction and dissolution processes as well as tribology. In many of these applications, the interface of the IL with its environment (gas, liquid, solid) plays an important role. Therefore, knowledge about interface properties and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. The majority of previous studies mainly focused on non-functionalized ILs; thus the knowledge about the influence of functional groups on the surface composition is still scarce. We present a systematic study addressing the surface behavior of a variety of functionalized and also some non-functionalized ILs [1]. From angle-resolved X-ray photo-electron spectroscopy, detailed conclusions on the surface enrichment of the functional groups and the molecular orientation of the cations and anions are derived. The systems include imidazolium-based ILs methylated at the C(2) position, a phenyl-functionalized IL, an alkoxysilane-functionalized IL, halo-functionalized ILs,
thioether-functionalized ILs, and amine-functionalized ILs. The results are compared to the results for corresponding non-functionalized ILs, if available. Generally, an enrichment of the functional group at the surface is only observed for systems which have very weak interaction between the functional group and the ionic head groups.


Coll 521

Oil-soluble ionic liquids as next-generation lubricant antiwear additives

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Here we review our recent development of ionic liquids (ILs) as next-generation ashless anti-wear (AW) additives, specifically for IC engine lubrication. The designed oil-soluble ILs are generally composed of quaternary-structured cations and surfactant-type anions, both of which contain long-chain alkyls. Our IL screening criteria included oil solubility, thermal stability, corrosiveness, wettability, and most importantly wear protection and friction reduction functionality. The top candidate ILs have exhibited superior AW characteristics compared to conventional zinc dialkyldithiophosphates (ZDDP) and ashless amine-phosphates. Comprehensive characterization has correlated the AW mechanisms of ILs to their unique physical and chemical interactions with metallic bearing surfaces. The first prototype IL-additized low-viscosity engine oil has demonstrated a >2% improved fuel economy and comparable engine wear protection benchmarked against the Mobil 1 SAE 5W-30 oil in full-size engine dynamometer tests. In addition, accelerated catalyst aging tests suggest that the IL may potentially have less adverse impact than ZDDP on three-way catalysts.

Coll 522

Structurally evolving "flat solid"/oil interfacial self assembled surfactant structure steadily enforces peculiarities into oil spreading behavior

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Spreading behavior of oil (hexadecane) droplet on flat copper surface was studied with oil having surfactants of different head groups and varying chain lengths. The droplet spreading rate decreased with increase in either surfactant [Triphenyl phosphorothonate (TPPT)] concentrations (0-2 wt%) or chain lengths (TPPT, butyl and nonyl TPPT). Within an intermediate (0.01%-2 wt%) concentration range, the manner in which spreading rates decreased was different with increase in chain lengths; two
spreading regimes with different spreading rates, and a cross over regimen in between. At certain surfactant concentration, the initiation of the crossover regimen occurred faster for longer chains. Such behavior was also observed with surfactants having different head groups, e.g., dodecylamine surfactants induced reduction in spreading rate spontaneously [in a few (< 15 seconds) seconds exhibited pinning] as compared to several (> 10 mins) minutes for dodecanol. Such inconsistency in terms of different time frames in which spreading rate varied entailed the role of the forces (FSASS) exerted from an evolving interfacial [solid/oil (S/O) and solid/oil/air (S/O/A)] self assembled surfactant structure (SASS) over the viscous and surface tension forces. Structural evolution of SASS has been correlated to the adsorption affinity of the surfactants by virtue of its head group functionality, and arrangement including a rearrangement step. While higher (e.g., dodecylamine) adsorption affinity of surfactants enables faster SASS formation activating FSASS early on, a rearrangement step correlated to an increase in FSASS ensuing pinning of the droplets, where FSASS is significant enough to counter balance the viscous/surface tension forces. Furthermore, it appears that there exists a rearrangement (packing) step during which the FSASS increases further leading to contraction of a droplet. SASS distributions across the S/O and S/O/A interface, if are in patches across the interfaces, created regions with different spreading powers, as FSASS is less effective in the patchy regions, and thus, leading to specific spreading behaviors such as protruding edges along the contact line, formation of dewetted regions across the S/O interface and even droplet spreading outwards with a dewetted region in the middle can also be seen.

**COLL 523**

**Structure and lubricity of ionic liquids in the presence of water**

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Ionic liquids (ILs) are known to have remarkable properties including vanishingly low vapor-pressures, are non-flammable, and have wide thermal and electrochemical stability windows that make them ideal for several applications. The nanoscale properties of ILs are also favorable for lubrication. Several studies have demonstrated the layered structure of ILs in nanoconfinement and how this structure can aid in reducing friction: The confined ions resist being "squeezed out" when surfaces are compressed, with the result that an IL film remains between the surfaces up to high pressures, thus preventing direct contact.

We have investigated the ion dynamics within hydrophilic nanocontacts by combining experiments with MD simulations. We show how IL composition and water influence speed- and load-dependence of shear in the selected hydrophilic nanocontacts exposed
to 0% and 37% RH. Both the presence of water and the alkyl-chain length of the imidazolium cation were found to influence the equilibrium structure of the nanoconfined film, and its dynamic properties. We have identified a change of ion-pair orientation and slip condition for film-thickness transitions, i.e. on the resistance of the IL-layers to being squeezed out from the contact, induced by adsorbed water. A boundary-film lubrication regime with lowest friction, an intermediate lubrication regime that particularly depends on the IL-anion and an iso-viscous rigid hydrodynamic lubrication regime (with Newtonian fluid-film behavior) have been identified. The simulation in the boundary lubrication regime is consistent with the experiments and help elucidate the origin for the friction response. These findings should be taken into account in the design of ILs with good lubricant properties for specific applications.

**COLL 524**

**High vacuum tribometry tests of fluid lubricants on bearing steels**

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High vacuum tribometry tests, employing the ball on flat contact geometry, are being conducted for bearing steels (e.g. 440C) lubricated with low vapor pressure fluid lubricants used in spacecraft reaction wheel assemblies (RWA) and control moment gyroscope (CMG) bearings. The impetus for this work is to gain insight into whether or not such tribological systems have a propensity to develop a starved contact; through either interfacial interactions (dewetting) or adlayer fluid entrainment barriers. To date, tribometry tests have shown that decomposition of Pennzane based lubricants results in polymeric materials depositing adjacent to the contact on both the steel ball and flat. Unexpectedly, on both surfaces the deposited adlayers were found to exhibit a distinct deposition pattern that is anticipated to reflect the lubricants reflow field within the meniscus. Adlayer thickness measurements and the use of an N2 blow off jet to qualitatively examine the local adlayer-lubricant interaction will also be discussed.

**COLL 525**

**Effect of surface nanostructure and ion structure on the nanotribology of the graphite: Ionic liquid interface**

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Ionic liquids nanoscale properties make them potentially excellent lubricants: as the ions interact strongly with oppositely charged surfaces, they resist ‘squeeze out’ as surfaces are compressed, meaning a lubricating film will remain in place up to higher forces than
for a comparable molecular liquid. The lubricating properties of ionic liquids can be controlled by varying the molecular structure of the ions\textsuperscript{1-4} and by applying an electric potential to the sliding contact.\textsuperscript{3,5} In this work the lateral structure of the graphite ionic liquid interface is elucidated using combined high resolution amplitude modulated atomic force microscopy (AFM) imaging combined with quantum mechanical simulations as a function of potential. AFM nanotribological measurements will be rationalised in light of the surface and near surface ionic liquid nanostructure, and the molecular structure of the ions, to elucidate energy dissipation pathways. As the composition of the ion layer in contact with the graphite substrate changes as the potential is varied (anion rich at positive potentials and cation rich at negative potentials) this means that the relative contribution to each ion to lubrication can be commented upon. The variation in shear force with changes in the structure of the ions will be described, which enables the most lubricating ion morphologies to be identified.

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COLL 526

Nature and implications of near-perfect nanoparticle seeds

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Control over nanoparticle shape and size is commonly achieved via a seed-mediated approach, where nanoparticle precursors, or seeds, are hypothesized to template epitaxial growth. Despite the intimate relationship this suggests between seed structure and that of the final nanoparticle, structural control and characterization of the initial distribution of seeds are limited. We have found that an iterative reductive growth and oxidative dissolution process systematically controls seed structural uniformity. Further, we use this platform to study the implications of seed structure on: (1) the uniformity of gold anisotropic nanoparticles grown from them, (2) the ability to accurately determine
physical properties of nanoparticles with well-established structures, and (3) the extent of ordering in nanoparticle crystallization. Importantly, this attention to seed uniformity improves noble metal nanoparticle uniformity and purity to unprecedented levels for eight different shapes produced from the same seed source, which enables particle optical extinction coefficient measurements and micron-size superlattice assembly.

COLL 527

Control over the surface states of gold nanoparticle via the electronic properties of the ligand set

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Thiol-protected gold particles smaller than about 3 nm in diameter possess large magnetic moments, which can be observed via SQUID. These states are thought to arise, in part, from the S-Au-S "staple" motif that is present at the surface of thiol-protected gold. This motif is also strongly reminiscent of classic coordination chemistry complexes, and suggests that the nature of this magnetic state should be dependent upon the nature of the attendant ligands. Here, we demonstrate that the magnetic properties of these gold nanoparticle are, indeed, influenced by the nature of the ligands. In particular, we demonstrate that the magnetism is dependent upon both the binding mode and the inductive strength of the attached ligands. We demonstrate these effects via both SQUID and epr, and the connect trends in the magnetism to other observable effects, such as Raman scattering, electronic absorptions, electrical conductivity, and luminescence.

COLL 528

Looking at biomolecules on gold nanocrystal surfaces

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The nano-bio interface is of increasing interest for chemical sensing, imaging, and therapeutic applications that rely on nanocrystals as the sensing/imaging/delivery/therapeutic agent. In this talk I will discuss our latest work on understanding the relative amounts, conformation, and orientation of biomolecules that are adsorbed to gold nanocrystal surfaces in aqueous solution.

COLL 529

Characterization of the ligand shell of noble metal nanoparticles and applications to sensing
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In this talk the characterization of mixed ligand coated gold and silver nanoparticles will be presented. Advanced in scanning tunneling microscopy imaging of mixed ligand striped and Janus particles will be discussed. The role of the ligand shell structure in the ability of these particles to bind selectively to ions and small molecules will be presented.

COLL 530

Determining the mechanism of plasmon-driven reactions with time-resolved surface-enhanced Raman spectroscopy

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The use of plasmonic materials to drive chemical reactions represents an exciting approach in the development of efficient light-driven energy storage and conversion devices. A mechanistic understanding of photoreactions occurring at plasmonic surfaces is currently lacking, but is likely to involve some combination of hot electron transfer, highly localized temperature gradients, and/or modification of excited state potential energy surfaces.

We discuss our efforts to directly follow structural changes in reacting molecular plasmonic systems through the use of time-resolved surface-enhanced Raman spectroscopy (TR-SERS). TR-SERS is a pump-probe technique which provides ultrafast structural information on reacting molecules following plasmon excitation.
This talk will focus on our current efforts in using the TR-SERS technique to determine the mechanism of two plasmonically-enhanced chemical reactions: photoisomerization in a push-pull azobenzene, and light-driven organic pollutant degradation. In both systems, we investigate the role of hot electrons in driving the photochemistry on the timescale of the fundamental bond-stretching and bond-breaking processes. By obtaining time-resolved structural snapshots of these reacting molecules, the impact of the plasmon on the reaction rate, coordinate, and yield is determined.

The development and application of this highly-enhancing, surface-specific ultrafast spectroscopic technique provides a molecular-level understanding of the effect of excited plasmons on proximal chemical reactions. We anticipate our results should lead to design insight into efficient and cost-effective plasmonically-enhanced devices for energy harvesting, storage, and conversion.

**COLL 531**

**Double emulsions and colloidosomes-in-colloidosomes using silica-based Pickering emulsifiers**

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Poly(ethylene imine) (PEI) has been adsorbed onto the surface of fumed silica particles at pH 10 in order to produce an effective 'hybrid' Pickering emulsifier. Systematically increasing the PEI/silica mass ratio modifies the particle surface sufficiently to stabilize oil-in-water (o/w) Pickering emulsions using a fixed silica concentration of 1.0% w/w in conjunction with an aldehyde-rich multi-component oil via homogenization at 12 000 rpm for 2 min at 20 °C. Further increasing the PEI/silica mass ratio leads to phase inversion, producing water-in-oil (w/o) Pickering emulsions. Thus this system allows formation of stable water-in-oil-in-water (w/o/w) double emulsions using two batches of hydrophilic and hydrophobic PEI/silica hybrid particles that differ only in their PEI/silica mass ratios employed prior to homogenization. Stable w/o/w double emulsions can be prepared with oil volume fractions ranging from 5 to 42 %. Moreover, controlling the volume fraction of the w/o Pickering emulsion homogenized in the presence of an aqueous dispersion of the hydrophilic PEI/silica hybrid particles allows the mean diameter of the resulting oil droplets to be conveniently controlled between 20 and 160 μm. Fluorescence microscopy studies confirm that controlling the mean diameter of these oil droplets allows encapsulation of either single or multiple water droplets within them. Although these double emulsions do not require cross-linking at either interface to withstand an alcohol challenge, epoxy-amine cross-linking between the physically-adsorbed PEI chains and either an oil-soluble or a water-soluble bis epoxy-based polymeric cross-linker can be achieved to produce novel colloidosomes-in-colloidosomes, which may offer payload retention benefits over conventional colloidosomes.
Near-monodisperse 1.0 µm silica particles are surface-modified using 3-(trimethoxysilyl)propyl methacrylate (MPS) and subsequently coated by aqueous deposition of an ultrathin polypyrrole (PPy) overlayer to produce PPy-coated silica particles. The targeted degree of MPS modification and PPy mass loading were systematically varied to optimise the colloidal stability and PPy coating uniformity. MPS surface modification was characterized by contact angle goniometry and the PPy overlayer uniformity was assessed by scanning electron microscopy. HF etching of the silica cores produced hollow PPy shells, thus confirming the contiguous nature of the PPy overlayer and the core-shell morphology of the original particles. Four-point probe measurements and XPS studies indicate that the electrical conductivity of pressed pellets of PPy-coated silica particles increases with PPy surface coverage. Colloidal stabilities of the bare, MPS-modified and PPy-coated silica particles in aqueous solution were assessed using disk centrifuge photosedimentometry. MPS surface modification results in weak flocculation, with subsequent PPy deposition causing further aggregation. In contrast, white light aerosol spectrometry indicates a relatively high degree of dispersion for PPy-coated silica particles in the gas phase. Such PPy-coated silica particles are expected to be useful mimics for silica-rich micrometeorites and may also serve as a model highly absorbing aerosol. Advanced. Functional. Materials. 2014 , 24, 1290
The synthesis of ordered mesoporous silicas and organosilicas templated by Pluronic block copolymers is typically performed under quite strongly acidic conditions (for instance, 0.5-2 M aqueous HCl). It was recently recognized that lower acidity (~0.1 M HCl) offers unique opportunities in generating periodic mesoporous organosilicas (PMOs) with hybrid inorganic-organic frameworks and with spherical mesopores of high volume and large size. Highly ordered face-centered-cubic phenylene-bridged and ethylene-bridged PMOs templated by Pluronic F127 surfactant were successfully obtained with large unit-cell sizes, appreciable ordered mesopore volumes, and large pore diameters. The pore size tailoring has been explored for these PMOs. The synthesis of face-centered cubic ethylene-bridged PMOs with large pore volumes, which was reported earlier by others, was adapted to the use of a more cost effective and convenient framework precursor. Other organosilicas were also obtained under these conditions. The opportunities in the adjustment of the pore accessibility have been explored.
Anisotropic inorganic-organic core-shell hybrid nanowires for hybrid solar cells

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Inorganic-organic hybrid photovoltaics offer a cost-effective alternative to traditional inorganic solar cells. The electronic devices can be fabricated from solution using industrially viable printing and coating techniques. The ideal hybrid photovoltaic device possesses an ordered bulk heterojunction in which the polymer donor and the inorganic acceptor domains are vertically aligned to the electrodes to form periodic patterns. However, it is challenging to produce such an ordered structure in a manner compatible with solution-based fabrication. Here, we report novel hybrid inorganic-organic core-shell nanowires with precise control of interface via covalent bonding of side-functionalized conjugated polymers onto inorganic semiconductor nanowires. The resulting anisotropic nanohybrids serve as the photovoltaic elements and could be vertically aligned using traditional screen-printing. The structure-property correlations will be addressed.

COLL 535

Fabrication of thermally stable rod-shaped (BaSr)O-SiO2 core-shell particles for oxygen separation

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Oxy-fuel combustion is counted as one of the most promising technologies for capturing CO2 from power plants. However, it requires a massive amount of pure oxygen. Among oxygen-selective materials, the high capacity and selectivity of BaO is very attractive in oxygen separation, if the thermal stability and oxygen partial pressure for the transition of BaO redox reaction are improved. Therefore, in the present study, the thermal stabilization of BaO-BaO2 with high oxygen transition pressure was attempted by using a core-shell structure and incorporating Sr in the core, in which the rod-shaped core particles of (BaSr)O was coated with the porous silica (SiO2) which was thermally and chemically stable and highly compatible to core materials. That is, the uniform rod-shaped (BaSr)CO3 single crystals with controllable composition were first prepared by co-precipitation with modifier of Mg2+ in aqueous media. Then, the smooth and homogeneous SiO2 shell was built on the core particles to form the (BaSr)CO3-SiO2 core-shell structure by a modified Stöber method, in which CTAB was used as structure-directing templates for the polymerization of silicates and also provide a mesoporous pathways in the SiO2 shell when it was removed. During fabricating SiO2 shell layer, the layer thickness was controlled from 20 to 200 nm via adjusting the concentration of TEOS. Then, the (BaSr)CO3-SiO2 core-shell particles were calcinated under H2 environment for conversion to the porous (BaSr)O-SiO2 core-shell rods. In this structure, the porous SiO2 shell thermally stabilized the active (BaSr)O cores and also allowed a rapid transport of oxygen gas during the redox reaction at a high operating
temperature. In addition, the oxygen partial pressure for transition of BaO redox reaction sharply increases due to the incorporation of Sr in the core. As results, it was demonstrated that the core-shell structured (BaSr)O-SiO₂ rods would highly be worth for massive oxygen separation.

**COLL 536**

**Triemethoxysilylpropyl(polyethylenimine) mediated one-pot synthesis of silica-coated metallic nanoparticles**

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Metallic nanoparticles are known to be efficient and highly active catalysts but they can often coalesce or precipitate if not protected.[1] To circumvent such a situation multistep surface modifications have been carried out in presence of coordinating polymers, ligands, or surfactants. However, such stabilizing agents strongly passivate the nanoparticle surface, causing a negative impact upon their catalytic activity.

In this work, we present a synthetic scheme which can provide reduction, stabilization, and protection in one step. Polyethyleneimine (PEI) is one of the most extensively studied polymers due to its iconic nature as well as its highly effective reducing and stabilizing capabilities. Therefore, we investigated a silylated PEI, trimethoxysilylpropyl(polyethylenimine) (TMSP-PEI), which was found to reduce, stabilize, and protect gold and silver nanoparticles in both aqueous and organic solvents without need of additional reducing agents. Upon further experimental analysis, it was discovered that adjustments to metal-ligand ratio produced different nanoparticle shapes. It has been shown that nanoparticles shapes can influence their catalytic activity thereby providing customizable applications.[2] Therefore, the synthesized nanoparticles were analyzed by TEM, SEM, IR, and a comparative analysis of their catalytic activity was assessed.


**COLL 537**

**Molecularly imprinted hydrogel photonic crystals for fast detection of glucose**
Nanogels self-assemble into hydrogel photonic crystals that have periodical and repeated unit structure with nanometer scale. Due to the stimuli-responsive optical properties, hydrogel photonic crystals have been used in clinical diagnosis, optical switches, biosensors, and chemical sensors. Here we synthesize poly(N-isopropylacrylamide-co-N-(2-hydroxyethyl)acrylamide-co-4-vinylphenylboronicacid)(poly(NIPA-HEAA-VPBA)nanogels by using emulsion precipitation polymerization. After the dialysis of the nanogel dispersions, poly(NIPAM-HEAA-VPBA) nanogels self-assemble into hydrogel photonic crystals. Crosslinker divinyl sulfone is reacted with the hydroxyl group of the nanogels to chemically stabilize the crystal structure of hydrogel photonic crystals including an imprinted template of glucose, resulting in molecularly imprinted hydrogel photonic crystals. Our results show that the photonic crystals have a fast response to glucose and a high selectivity and absorb glucose up to 4.2 mg/g. The molecularly imprinted hydrogel photonic crystals display a recognition behavior through the change of diffraction wavelength. As a concentration of glucose increases from 0 mol/L to 0.01 mol/L, the photonic crystals have 80 nm red-shift of diffraction wavelength. The molecularly imprinted hydrogel photonic crystals will promise to become a novel biosensor to monitor the change of glucose in human body.

COLL 538

Transparent and ultrastrong synthetic wood through bio-inspired LbL assembly

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This work presents new nano-composites possessing multiple interesting properties: strength, transparency, self-healing and biodegradability. Nature makes multi-property materials that gain their strength and functionality from the precise assembly of hard anisotropic particles embedded in a soft matrix. Despite intense research in the last years, the production of low defect bio-inspired nanostructures leading to composites with complex properties is still a challenge. Layer-by-layer (LbL) assembly pioneered and developed by our team since the early 90's allows the construction of hybrid architectures with controlled nanoscale composition and architecture. We used LbL assembly to prepare micron thick wood-inspired films using microfibrillated cellulose (MFC) and polyvinylamine (PVAm). In these transparent nano-structured films the in-plane orientation of cellulose fibers yields materials whose Young's modulus and strength surpass those of spruce, the wood from which MFC is produced. We will discuss how the deposition parameters control the layer growth (from 9 to 55 nm per layer pair), the composition, and the mechanical properties of the nano-composite films.
Experiments on the plasticizing effect of water also evidenced that hydration can turn a strong and brittle film (Young's modulus of 16Gpa) into a soft and ductile material (Young's modulus of 0.1GPa) and enable self-repair.

(A) Mechanical properties of some cellulose based materials. (B) Photograph of a 3.8μm thick synthetic wood film, edges are outlined for clarity.

COLL 539

Aldehyde capture ligation: A chemoselective approach to peptides and bioconjugates

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Chemoselective reactions for amide bond formation have transformed the ability to access synthetic proteins and other bioconjugates through ligation of fragments. In these ligations, amide bond formation is accelerated by transient enforcement of an intramolecular reaction between the carboxyl and the amine termini of two fragments. Building on this principle, this talk will describe an auxiliary-based approach called “aldehyde capture ligation (ACL)” that parleys the chemoselective reactivity of aldehydes and amines to enforce amide bond formation between unprotected peptide segments. This talk will demonstrate the application of ACL in synthesis of hybrid materials.
Non-cytotoxic smart fluorescent core/shell nanoparticles and their application in cancer therapy

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Responsive nanoparticles were obtained by growing poly(N-isopropyl acrylamide) ((PNIPAM)) and copolymers derived from poly(ether oxide) monomers (MO2MA, HOEGMA) at different rates by a controlled radical polymerization (ARGET-ATRP) from quantum dots (QDs) surfaces.

Each step of the synthesis process was monitored by the combination of different techniques like FT-IR, fluorescence, transmission electron microscopy, etc. The influence of the polymerization time or monomer rate on the final photophysical properties of the nanomaterials were studied by fluorescence spectroscopy.

The temperature responsive behavior of the ZnO/(co-)polymer nanohybrids was studied by Dynamic Light Scattering (DLS) and fluorescence spectroscopy.

The drug loading and release capacity and cytotoxicity of poly(ether oxide) derivatives core/shell NPs towards cancer cells were evaluated. Results obtained demonstrate the influence of the co-polymer structure for cancer therapy application.

Oxidative dehydrogenation catalyzed by Lil

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I will present experiments and ab initio molecular dynamics simulations of the oxidative dehydrogenation of propane to propylene with two different catalysts: molten lithium iodide and gas-phase iodine. I will also discuss in more general terms the idea of using molten halides as catalyst promoters or as catalysts.
Chemical reactions on surfaces play a critical role in many technologies and industrial processes such as catalysis, batteries, fuel cells and pollution cleanup. Detailed mechanistic and kinetic understanding of the surface chemical reactions is critical to further optimize and design new more efficient technologies. Microkinetic models that can accurately predict catalytic reaction rates require estimation of the equilibrium and rate constants for different elementary reaction steps involving adsorbed species.

Rate constants for surface reactions are often estimated using DFT combined with saddle-point finding methods (e.g., NEB) and harmonic transition state theory (HTST), which assumes that all adsorbates are localized harmonic oscillators with only vibrational modes. We show here that this harmonic oscillator approximation significantly underestimates the entropies of many adsorbed species, which were recently found experimentally to be almost 2/3 of the entropy of their gas-phase analogues, due to large contributions from nearly free translations and rotations of the adsorbates parallel to the surface. Knowing these entropies is necessary for accurately estimating the pre-exponential factor in their rate constants.

Here we combine DFT calculations and the Hindered Rotor Density of States Interpolation Function of McClurg, Flagan and Goddard to predict the entropy associated with rotations and translation of adsorbates parallel to the surface for a range of temperatures. This allows us to more accurately estimate the partition functions, entropies and kinetic prefactors for adsorbates at catalytically relevant temperatures, in better agreement with experimental data.


**COLL 543**

**Role of molecular structure in surface chemical reactivity**

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Because the surfaces of small structures can dominate their properties, implementing functional nanoscale materials depends to a large extent upon understanding and
controlling the surface reactivity. This talk will focus on studies of the adsorption and reaction of organic molecules at semiconductor surfaces toward the ultimate goal of providing new chemical functionality to a substrate. The presentation will examine the role of molecular structure in controlling the product distribution upon adsorption of bifunctional molecules on the Ge(100)-2x1 surface. The adsorption of various structural and stereoisomers of diamines and diols was studied using a combination of experimental (infrared spectroscopy, X-ray photoelectron spectroscopy) and theoretical (density functional theory calculation, Monte Carlo simulation) methods. The diamines (cyclohexanediamine, phenylenediamine) adsorb by a combination of N-H dissociation and N-dative bond formation, whereas the diols (benzenediol) adsorb by O-H dissociation. In each case, however, not all of the functional groups react, with the unreacted fraction depending on the isomer. The results reveal the interplay between electronic and geometric structure in determining product distributions in the adsorption of bifunctional molecules at the semiconductor surface.

COLL 544

Understanding TiO₂ surface chemistry using theory and experiment

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In this presentation we illustrate the interplay between theory and experiment to elucidate key processes over TiO₂, particularly redox reactions between surface and adsorbates, and photo-decomposition of organic species. We utilize a combination of density functional theory, scanning tunneling microscopy, and a variety of other experimental tools in this work. TiO₂ is a prototypical metal oxide material for surface science and catalytic studies, and advances in understanding this material are crucial. We show how surface and near-surface defects (which reduce the surface or provide unpaired electrons) as well as photo-excited electrons may interact with adsorbates to influence adsorption strength. We also examine O₂ adsorption and dissociation as the O₂ interacts with excited electrons. Our studies show that the presence of these unpaired electrons is crucial for much surface chemistry, and that surface (or near-surface) defects must be considered when working with TiO₂ and many metal oxides. We also examine photo-decomposition of adsorbed ketones, and use theory to explain the experimentally-observed reaction pathways for the ketones.

COLL 545

Imaging surface reactions of acetone and formaldehyde on TiO₂

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Acetone and formaldehyde are involved in many surface catalytic and photo-catalytic reactions on metal oxides. We studied surface reactions of acetone and formaldehyde on TiO₂ surfaces using variable-temperature scanning tunneling microscopy (STM) and density functional theory. On rutile TiO₂(110), we find that both acetone and formaldehyde prefer to adsorb molecularly on the bridging bonded oxygen (Ob) vacancy (VO) sites. The isothermal time dependent images show that acetone and formaldehyde have different diffusion channels. Calculated potential energy profiles provide detailed insights on reaction mechanisms. To understand surface reaction processes on anatase TiO₂, we have studied the atomic structure of anatase TiO₂(001) epitaxial thin films grown by oxygen plasma assisted molecular beam epitaxy. In situ reflection high-energy electron diffraction, X-ray photoelectron spectroscopy, and ex situ STM were used to characterize the structure of (1x4) reconstructed anatase TiO₂(001) surfaces. High resolution STM images show that the atomic corrugation of the bright row on the surface is not uniform and is highly bias voltage dependent. We propose a modified added molecule model for the anatase TiO₂(001) surface structure.

COLL 546

Computational studies of methylaluminoxane (MAO) oligomers with magnesium chloride surfaces

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Methylaluminoxane (MAO) is one of the most commonly utilized co-catalysts for the activation of metallocenes in single-site olefin polymerization. Supporting MAO on MgCl₂, silica, or alumina surfaces dramatically decreases the aluminum to catalyst ratio required for good activities. However, little is understood about the structure(s) of MAO, its interaction with the support, and the mechanism of heterogeneous polymerization. Density Functional Theory calculations were carried out at the Generalized Gradient Approximation level using D3 dispersion correction (i.e., revPBE+D3) to investigate the interaction of a few relevant models for MAO with the (100) and (110) surfaces of MgCl₂. The bonding energy between the species likely to be present in a MAO mixture and the finite slabs were calculated to be large (≥ 40 kcal/mol). Furthermore four-coordinate Mg, in MgCl₂ (110), interacts more strongly with MAO species than five-coordinate Mg, the (100) slab. MAO cage structures can interact with the (100) surface via either Al-μ-Me-Mg and O-Mg bonds, whereas on the (110) surface Al-Cl bonds are also formed. The decomposition of the deformation density caused by these surface-adsorbate interactions was analyzed with ETS-NOCV (Extended Transition State method with the Natural Orbitals for Chemical Valence theory). This confirms that the most important orbital interactions contributing to ΔEoi are: Al-μ-Me-Mg, Al-Cl and Mg-O bonds. Finally, even though the (AlOMe)₁₂ cage-like structure (MAO₁₂,c) does not have strained bonds with high latent Lewis acidity, the binding via methyl groups allows this species to interact with the MgCl₂ surface more strongly than (AlOMe)₁₂ in the nanotubular form (MAO₁₂,n). On the other hand supported [MAO₁₂,n·AlMe₃], and other trimethylaluminum-
bound species are energetically preferred over MAO\textsubscript{12,c} on both the (100) and (110) surfaces, with the fully saturated nanotube ([MAO\textsubscript{12,n·4}AlMe\textsubscript{3}]) being the most stable.

**COLL 547**

**Teaching old antibiotics new tricks**

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By examining the mechanism of membrane permeation in a range of molecules that control membrane topology, including antimicrobial peptides, cell penetrating peptides, and viral fusion peptides, we show how a combination of geometry, coordination chemistry, and soft matter physics can be used to approach a unified understanding of the amino acid sequence requirements of membrane permeation. Using these ideas, we demonstrate that it is possible to renovate old antibiotics by adding new functions. In a parallel line of inquiry, we will also show how the multi-functionality of antimicrobial peptides can lead to auto-immune diseases such as lupus and psoriasis.

**COLL 548**

**Single-molecule resolution of protein structure and interfacial dynamics on biomaterial surfaces**

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A method was developed to monitor dynamic changes in protein structure and interfacial behavior on surfaces by single-molecule (SM) Förster resonance energy transfer (FRET). This method entails the incorporation of unnatural amino acids to site-specifically label proteins with SM-FRET probes for high-throughput dynamic fluorescence tracking microscopy on surfaces. As demonstration of this method, structural changes in the protein organophosphorus hydrolase (OPH) were monitored upon adsorption on fused silica (FS) surfaces in the presence of bovine serum albumin (BSA) on a molecule-by-molecule basis. Analysis of > 30,000 individual trajectories enabled the observation of heterogeneities in the kinetics of surface-induce OPH unfolding with unprecedented resolution. In particular, two distinct pathways were observed; a majority population (~ 85%) unfolded with a characteristic time scale of 0.10 s, and the remainder unfolded more slowly with a time scale of 0.7 s. Importantly, even following unfolding, OPH readily desorbed from FS surfaces, challenging the common notion that surface-induced unfolding leads to irreversible protein binding. This suggests that protein fouling of surfaces is a highly dynamic process due to subtle differences in the adsorption/desorption rates of folded and unfolded species. Moreover, such observations imply that surfaces may act as a source of unfolded (i.e., aggregation-prone) protein back into solution. This approach has since been expanded
to investigate the interaction of fibronectin and biomaterial surfaces to understand the cellular response to foreign materials in vivo. Ultimately, this method, which is widely-applicable to virtually any protein, provides the framework to develop surfaces and surface modifications with improved biocompatibility.

**COLL 549**

**Characterizations of self-assembly of peptides and self-assembled peptide nanonetworks**

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Understanding of aggregation kinetics of peptides and characterization of intermolecular/intramolecular interactions during self-assembly of peptides into supramolecular networks can give new insights for development of functional biological systems. The interactions and dynamic aggregation kinetics of peptides can be analyzed via molecular dynamics simulations. Peptide based nanonetworks have also been investigated for numerous biomedical applications, including drug delivery, regenerative medicine and tissue engineering. Our research aims to understand network interactions involved in releasing small molecules from peptide nanonetworks, and establish a model for their mass transport behavior and controlled cellular responses with respect to released molecules. In this work, transport behavior of the peptide nanonetworks were investigated experimentally at nanoscale and diffusion coefficients of the small molecules were estimated using semi-empirical methods. Development of an engineering model to translate the effects of physical interactions into predictable diffusion coefficients and mass transport behavior can aid researchers in building scaffolds for controlling cellular responses.
Responsive polymer surfaces for controlled cell adhesion

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Responsive surfaces are able to switch their properties in response to a stimulus or change in the environment. Switchable surfaces composed of grafted polymers are capable of dynamic switching and may, therefore, be favorable for applications in self-cleaning surfaces, life sciences, and cosmetics. The switching mechanism in such responsive systems is realized via molecular reconstruction of polymer chains governed by the thermodynamic principle of surface energy conservation.

We synthesized hybrid molecular brushes (HMB) by grafting hydrophilic polyacrylamide and hydrophobic polystyrene side chains onto a backbone of chitosan. Chitosan is an abundant biopolymer inexpensively derived from natural sources. Chitosan possesses unique properties that allow for convenient grafting by radical polymerization. Also, it is rich in other functionalities that allow for simple immobilization on different surfaces.

We show that chitosan HMB can be immobilized on the substrate surface using multi-site polymer monolayer attachment or through quasi-reversible adsorption of the
backbone. Immobilized HMB demonstrate outstanding response to the changes in the environment as demonstrated by micro-adhesion and contact angle measurements.

We used several prokaryotic cell lines (Escherichia coli DH5α and Salmonella typhimurium LT2) as a model to study the mechanism of bio-adhesion to such responsive surfaces. The cells are transformed with a plasmid containing a lux operon that is modified to create its own substrate for bioluminescence of the luciferase gene. Our results show that the cell adhesion can be efficiently controlled by external stimuli such as pH or Red-Ox potential. Further analysis of the cellular fimbria which attach to the surface will allow a better understanding of the mechanism of cell adhesion.

COLL 551

Controlling lipid membrane conformations on nanograting structured supports

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Many studies have attempted to span supported lipid bilayers (SLBs) over nano-structured to create free-standing regions in SLBs for various biosensor applications. However, membranes following the support surface contour are more frequently observed than are free-standing membranes on structured supports, and all otthe previously reported conditions to create free-standing membranes are case by case. A general guideline to choose suitable physiologically relevent conditions is necessary for the platforms to have broad applications. The objective of this study was to estimate the system energies of free-standing and contour-following membrane states, and determine which state is the most energetically favorable under various conditions. For a lipid membrane preferring to stay close to the support, an energy reward occurs when they are in close proximity; however, increasing the contact area on a structured surface can result in an energy penalty because of the bending of the lipid bilayer. Whether the energy reward or the energy penalty dominates could determine the membrane state.

We used the extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and the Helfrich bending theory to relate the energy sizes to experimentally controllable parameters. We experimentally examined whether the membrane state followed the model prediction when we used various buffer ionic strengths, various lipid types, and nano-grating supports with three different geometries. Because it is difficult to observe the experimental membrane state directly at the nano scale, we developed a method to use the fluorescence recovery shape change after photobleaching to distinguish experimental membrane states from micron scale. Our experimental results closely matched the theoretical predictions, suggesting that the developed model can be used to predict the suitable conditions for the formation of free-standing bilayers on nano-structured solid supports.
Human corneal stroma and Descement's membrane revealed by quantitative nano-mechanical atomic force microscopy at nanoscale

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The structures and mechanical properties of human tissues are significantly influenced by the environment condition and pathologic condition. The functionality of human cornea can be linked to the collagen fibers. In the work, morphological and mechanical property variations of different layers of human cornea, (stroma/Descement's membrane), have been revealed by quantitative nano-mechanical atomic force microscopy (QNM AFM). It is found that the collagen fibers in stroma tissues show the specific periodicity and the stiffness of giga-Pa magnitude in 40% humidity; however, under fully hydration condition, the collagen fibers clearly show nanoparticle structures along the fibers with the stiffness in mega-Pa magnitude. More interesting, the collagens in Descement's membrane mutated by the Fuch's endothelium dystrophy disease formed the super collagens, which had larger size and lower Young's modulus comparing to the normal ones. The interplay of structures and nanomechanical mapping can be applied for the future diagnosis and assessment or even pathologic analysis.
Evaluating protective low adsorption coatings by a simple and sensitive method

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The early-stage detection of numerous diseases is often critical to the success of patient outcomes. For this reason there is a great deal of activity towards the development of highly sensitive devices and assays that can detect very low concentrations of disease biomarkers. A critical need for all of these methods is to prevent the nonspecific adsorption of the biomarker onto surfaces before the sensing element is reached. The nonspecific adsorption of interfering proteins and other biomolecules onto the sensing element must also be prevented.

We describe a simple and sensitive method to evaluate the effect of different treatments on nonspecific adsorption. The method exploits the increase in sensitivity that is gained in small volumes. Using a model silicon chip containing picoliter wells, we report on the nonspecific adsorption of femtogram quantities of proteins and the effect of different surface treatments. This method should be applicable to any material that can be cast with picowells on its surface.

Utilizing size-dependent NSET as an optical probe for human telomere conformations

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Recent advances in Nanometal Surface Energy Transfer (NSET) theory provide versatility in the fields of cellular biology and biochemistry where flexibility in assay design is essential. Gold nanoparticle-based energy transfer assays utilized in biology often require a variety nanoparticle sizes to achieve increased surface payload or better cellular uptake, which has shown to be influenced by nanoparticle size. New size-dependent NSET calculations eliminate the one-dimensional “on-to-off” premise of energy transfer probes in biology, and provide intensity-based distal measurements between an organic dye fluorophore and a larger gold nanoparticle quencher. Here we demonstrate the versatility of NSET in biochemical assays by monitoring the G-quadruplex folding of dye-labeled human telomere sequences on various sizes of gold nanoparticles. Appropriate quenching by the gold nanoparticles based upon size-dependent NSET theory for each telomere's folding is observed, in that larger gold sizes reduce the photoluminescent of the dye and shorten the lifetime. Correlation of distal measurements in the folded G-quadruplex conformation on multiple gold nanoparticle
sizes confirms that the nanoparticles do not influence the native conformational behavior of nucleic acid biomolecules appended to the surface. These functional NSET designs also provide insight into rational probe designs for other conformation-based biological events.

**COLL 555**

**Nanoelectronic detection with holey reduced graphene oxide**

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Because of graphene's unique physical and chemical properties, this nanomaterial has been widely explored for many applications in different fields of science and technology. However, graphene has a zero-bandgap electronic structure, which limits its applications in semiconducting devices such as field-effect transistors (FETs). To overcome this limitation, material chemists have synthesized graphene with smaller sizes and different shapes, namely graphene quantum dots and graphene nanoribbons, which lead to bandgap opening in these nanocarbons because of quantum confinement and edge effects. Carbon nanotubes, on the other hand, which have well defined semiconducting electronic structure, have been successfully employed in many FET-based chemical and biological sensors. However, covalent functionalization schemes required for sensor applications result in total loss of their electronic properties.

Recently, we have synthesized and explored sensor applications utilizing a new graphene derivative, holey reduced graphene oxide (hRGO), which can be visualized as an interconnected network of graphene nanoribbons. hRGO was synthesized via enzymatic oxidation, in which graphene oxide was treated with a mixture of horseradish peroxidase (HRP) and H$_2$O$_2$ followed by hydrazine reduction (1). This nanomaterial not only offers a high amount of oxygen moieties around the edges of the holes, which are required for effective covalent functionalization, but also retains good electronic properties. The aforementioned features represent a balance difficult to achieve with either graphene or carbon nanotube-based chemical sensors. When decorated with Pt nanoparticles, hRGO devices exhibited a large and selective electronic response toward hydrogen gas (2). In the most recent example, covalent functionalization of the oxygen moieties on hRGO with the antimicrobial peptide, Magainin I, produced a broad-spectrum bacterial probe for the detection of gram-negative bacteria that outperformed other tested carbon nanomaterials (3).


**COLL 556**

**Aqueous graphene dispersions: Optical properties and stimuli responsive phase transfer**
Stimuli responsive triblock surfactants and nanolatexes derived from reactive ionic liquids are demonstrated to be the most effect stabilizers reported for dispersing graphene at 1\% to 5\% by weight in water. These results surpass most reports by 10 to 1000-fold and result in long time (>6 month) stabilization. Optical data in the visible show that our dispersions are also predominantly single sheet and bilayer, as deduced from analysis of concentrated dispersions and from layer-by-layer coatings. The visible extinction at 500 nm in suspension is shown experimentally to be 49 cm\(^2\)/mg graphene, and this result is shown to be rigorously consistent with fundamental studies of macroscopic single-layer graphene and its fine structure constant, \(\alpha = \frac{e^2}{\hbar c}\). The mechanism of exfoliation is presented in terms of highly activated exfoliation with strong adsorption of stabilizer with \(\text{sp}^2\) graphene surfaces. Interesting controlled sedimentation, coating, rheo-optical, and phase transfer phenomena are demonstrated. These methods will make it possible to produce highly dispersed and concentrated graphene using scalable manufacturing methods.

**COLL 557**

**Multifunctional graphene oxide for label-free detection of circulating tumor cell from infected blood**

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Here we will discuss our recent report on the development of multifunctional graphene oxide for the ultra-sensitive label-free detection and separation of circulating tumor cell from infected blood sample. Our experimental data also shows that hybrid graphene oxide can be used for selective killing of cancer.

**COLL 558**

**Molecular and cell-level bio-adhesion to supported graphene sheets: The fundamental basis for interactions**

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The interactions between supported graphene sheets and biomolecules or cells are critical to sensing applications of graphene. Ongoing work focuses on the modification of graphene through chemical or physical modification. These efforts are complicated by process-related defects and contamination of the graphene surface. This work compares protein adsorption on graphene, glass, and plastic surfaces, with attention to
adsorption kinetics, adsorbed amounts, and protein retention in flow. The apparent extent of fibrinogen denaturing on graphene is compared to that on engineering and other model surfaces. Additionally addressed is the ability of graphene to quench a fluorescent label on the adsorbed protein, compared with the fluorescence reduction of the tracer in the interfacial environment near glass, where local pH influences fluorescent yield. Finally the adhesion of S. Aureus on graphene is compared with that on other model surfaces. It is demonstrated how the processing of graphene sheets can influence graphene's bacteriocidal character.

COLL 559

Exfoliated graphene monosheet WO$_3$-modified supercapacitors with high power density

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Supercapacitors, being recently under development for new applications in automotive, energy, military, and other industries, offer outstanding characteristics, such as the ultra-high specific capacitance, fast charging/discharging, enhanced safety, and low leakage currents. Extensive research has been carried out around the world to further improve these characteristics, especially the energy density, power density, and durability. In our studies, we have focused on the high power density supercapacitors with high specific capacitance and low internal resistance providing very fast charging and discharging. We have investigated the unique qualities of supercapacitors based on exfoliated graphene nanosheet (GNS) substrates and hybrid GNS-based supercapacitors with conductive polymer and redox metal-oxide pseudocapacitance components. The hybrid GNS/WO$_3$-x supercapacitor electrodes were nanoengineered using exfoliated graphene oxide reduced subsequently by cathodization in the presence of a H$_2$O$_2$-pertungstate complex and tested in sulfuric acid solution. The obtained electrode materials have been characterized using high-resolution SEM, AFM, Raman spectroscopy, and electrochemical methods. The GNS separation has been regulated with pseudocapacitance-element nanoparticle size enabling fine-tuning of the internal resistance and current collection capabilities of the supercapacitor electrode material. The addition of polyaniline (PAni) to the graphene intersheet space has been found to increase the specific capacitance and improve the device cycling durability. The charging/discharging curves, obtained for the assembled supercapacitors, have shown considerable enhancement of the supercapacitor power density in comparison with that of bare transition metal oxide devices.

COLL 560

Chiral resolution via single-atom-thick membranes: A new concept demonstrated on functionalized nanoporous graphene
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Enantiomeric forms of a drug molecule are known to vary in potency, toxicity and effect they might have on biological systems. Therefore, drug research and development demand to have enantiomers of all bioactive molecules separated and tested. We present a new, alternative method for the separation of racemic mixtures via single-atom-thick membranes, using functionalized nanoporous graphene as a template. Computational simulations based on density functional theory show that the attachment of a suitable chiral 'bouncer' molecule to the pore rim prevents the passage of the undesired enantiomer while letting its mirror image through. In contrast to common methods such as gas chromatography, high performance liquid chromatography and capillary electrophoresis, this allows an identification of a left- or right-handed drug molecule in a single molecular event.

COLL 561

WITHDRAWN

COLL 562

Modeling the filling of methane in heterogeneous pore networks

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Because of its relatively large and tunable pore sizes, mesoporous silicas are good candidates as catalyst supports in the production of biofuels. Understanding the transport properties of a material like SBA-15 with its secondary pore network of meso- and micro-pores is important in engineering useful catalyst systems. Contrast-matching small-angle neutron scattering (CM-SANS) studies showed that the SBA-15 micropore structure\textsuperscript{3} is consistent with cylindrical pores with an onset diameter of $\sim5.5$ Å. Quasi-elastic neutron scattering (QENS) data on methane in SBA-15 contains information about rotational and translation diffusivity in the pore network\textsuperscript{2} but can be hard to interpret because diffusion rate depends on pore size, temperature, and degree of filling. Here we present a simulation of pore filling of SBA-15 as a function of pressure at 77K. We follow a formulation of Rasaiah and coworkers\textsuperscript{3} to determine the chemical
potential of methane in different size pores and then construct probability distributions for methane filling in a network with a distribution of pore sizes. We discuss the use of molecular dynamics simulations for modeling the QENS data.

References


COLL 563

Analysis of the hydration thermodynamics of the proton

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The cluster-pair approximation (CPA) utilizes cluster and bulk thermodynamic data in estimating the hydration enthalpy and free energy of the proton. Here the CPA is analyzed from a quasi-chemical theory (QCT) perspective. The statistical mechanical analysis shows that a key assumption of the CPA leaves open the possibility of shifts between the proton values obtained by extrapolation of small cluster data and the actual large-system values. Numerical tests of the CPA are performed using the QCT, polarizable classical simulations (AMOEBA model), and quantum chemical calculations. The results indicate a small shift in the proton hydration free energy and a larger shift in the enthalpy relative to the previously accepted values. The resulting hydration entropy is consistent with the Marcus value. The electrochemical surface potential of water obtained in the analysis is roughly -0.4 V, but it is emphasized this widely discussed quantity can only be uniquely defined for single ions in modest-sized water clusters.

COLL 564

Coarse-grained simulations of shock wave - lipid bilayers interactions

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We used MARTINI coarse-grained force field to study poration of a lipid bilayer by a shock wave induced nanobubble collapse. We simulated different systems containing different number of nanobubbles and also systems with different sized nanobubbles that were exposed to shock waves propagating with different velocities. We observed creation of pores and damage to the bilayers. In some cases we observed recovery after the passage of the shock wave; nevertheless we observed that a large amount of
water crossed the pore that was temporarily created. We also observed systems where the pores had a permanent character.

**COLL 565**

**Microscopic reversibility: The organizing principle for molecular machines**

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The physical principles by which molecular machines function are very different than those governing the operation of even very small mechanical machines. Understanding these differences is leading to significant progress in the design and construction of machines that use chemical, electrical, mechanical, or light energy to carry out molecular tasks for nanotechnological applications. The analysis here shows that the essential principle for designing nano-scale energy converters is the combination of a catalytic function with an allosteric sensing function.

**COLL 566**

**Adsorption kinetics of complex fluids at liquid surfaces**

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The kinetics of adsorption of surface-active compounds to liquid interfaces plays an important role in many process including printing, coating, spraying, wetting and foaming. For simple surfactants, the adsorption processes are usually categorised as diffusion control, kinetic control or a mixed mechanism in which both diffusion and the local transfer from sub-surface to surface determine the adsorption rate. In complex fluids containing aggregates of surfactants, such as micelles or vesicles, or complexes of surfactants with each other or with polymers, the adsorption kinetics depend also on the composition and transport properties of the aggregates in the bulk phase and the rates of interchange between aggregates and monomers. In addition, there is the possibility of micelles or complexes adsorbing directly to the liquid surface, which then promotes the disintegration of the aggregate. This talk will present experimental data on the kinetics of adsorption of micellar solutions (of pure and mixed surfactants) and of polymer-surfactant mixtures to the air-water interface, principally in an overflowing cylinder. Simple theoretical models will be described that explain some features of the experimental data and outstanding questions will discussed. Areas for future theoretical development will be outlined.

“Effects of Bulk Aggregation on PEI/SDS Monolayers at the Dynamic Air/Liquid Interface: Depletion due to Precipitation versus Enrichment by a Convection/Spreading Mechanism” Angus-Smyth, A.; Bain, C. D.; Varga, I.; Campbell, R. A. Soft Matter, 2013, 9, 6103

COLL 567

Pushing atoms: Applications in nanoscience

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The convergence of nanotechnology with advanced molecular modeling has enabled radical new advances in single atom physics across diverse disciplines: High-speed, high-density electroniques, molecular biosensors, energy conversion, etc. This presentation explores the technologies involved in the generation of atomic manipulation and nanoscale devices.

More specifically, the unique fabrication processes required to realize a stochastic, nanopore sensor serves as a forum to discuss the anatomy of nanoscale innovations developed in the creation of new nanodevices and nanostructures.

The nanopore sensor presented here consists of a 1nm-10nm nanopore fabricated in a thin (40nm) membrane and articulated with graphene like nanoelectrodes at the
periphery. DNA is electrophoretically driven through the nanopore and “tunneling”
current between the electrodes is modified as different nucleotide sequence pass.
Single nucleotide counting has been achieved and will be presented, but focus is given
to the fabrication methods and challenges realizing the nanopore device.

**COLL 568**

**Ab molecular dynamics simulations of Pb(II) and selenite anions at the water-
goethite interface**

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We will report electronic structure modeling of lead, a toxic metal ion, sorption
on goethite surfaces, in the presence and absence of explicit water, and compare
the predicted structural properties to EXAFS data. Co-adsorption of selenite
will also be considered. This study is critical to predicting the retention duration of toxic ions in soil samples.

Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S.~Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

**COLL 569**

**New dimensions in patterning: Placement and metrology of chemical functionality at all scales**

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We place single molecules, as well as pairs, lines, clusters, and larger groups of molecules into precisely controlled environments on surfaces. Monolayer matrices and inserted molecules and sub-assemblies can be designed so as to interact directly, to give stability or other properties to supramolecular assemblies. The exposed interface can be engineered to control physical, chemical, electronic, and biological properties. New families of molecules, particularly upright, symmetric cage molecules, are being developed to yield even greater control and are enabling determination of the key design parameters of both the molecules and assemblies. This, in turn, is enabling hierarchically controlled chemical patterning and selective functionalization from the subnanometer to the centimeter scales. We are simultaneously developing a suite of metrology tools for these methods to give unprecedented information on the structures and properties of these assemblies.
**COLL 570**

**New nanostructures for increased selectivity and stability in catalysis and their characterization by infrared absorption spectroscopy**

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Several nanoarchitectures have been tested to add selectivity and stability to transition metal-based catalysts. Tetrahedral Pt nanoparticles have been used to selectively promote trans-to-cis catalytic isomerization in olefins. Encapsulation of metal nanoparticles in dendrimer and SAMs organic frameworks has been tried to improve on size distribution and to add enantioselectivity. The use of silica coatings and yolk-shell nanostructures has been explored as a way to minimize metal sintering. The performance of all these nanostructures has been evaluated by using infrared absorption spectroscopy, in both gas and liquid phases. Specifically, IR has been used in transmission mode to probe the diffusion of reactant through the different nanostructures under catalytic conditions, and in diffuse-reflectance (DRIFT) mode to follow the oxidation of CO promoted by yolk-shell nanocatalysts.

**COLL 571**

**Reactions on the edge: Catalytic chemistry at the metal-oxide boundary**

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A common structural motif in heterogeneous catalysis is the oxide-supported metal particle. While first-principles computational methods are well developed to represent the ordered surfaces of metals and metal oxides individually, in many cases catalytic activity is associated with the boundary of the two. Here protocols for constructing appropriate models are less well developed. In this work, we report density functional theory (DFT) results for a metal stripe model of this interface. We examine adsorption and reaction of species relevant to water-gas shift catalysis, a chemistry in which strong evidence exists for the role of this boundary in catalytic activity. We examine sensitivity of computational results to the model features. We show that the model interfaces exhibit reactivity features distinct from the individual components, that these differences primarily reflect the ability of adsorbates to communicate with the two distinct materials, and that results can depend sensitively on exact details of the model.

**COLL 572**

**Salt-induced self-assembly of bacteria on nanowire arrays**
With the development of integrated systems which seek to combine micro- to nanoscale structures with biological materials, the study of the chemical and physical interaction of biotic and abiotic components has gained pertinence. While previous research has focused on engineering anti-microbial surfaces against harmful pathogenic bacteria, the next generation of nano-bio hybrid systems require tuneable interactions to study and harness the potentially useful properties of biological cells. The field of bioelectrochemistry has arisen in recognition of this potential, and seeks to combine the optoelectronic properties of inorganic electrode materials with the synthetic and catalytic power of whole cells, such as bacteria. The acetogenic bacteria, *Sporomusa ovata*, has emerged as a model organism of bioelectrochemical synthesis for its unique ability to accept electrons from a polarized electrode in order to drive the metabolic reduction of CO₂ to acetate. Such a reaction is crucial to the development of systems for artificial photosynthesis, and for the renewable production of fuels and commodity chemicals from atmospheric CO₂. Due to the volumetric diffusivity of whole cell catalysts, high surface area electrodes, such as nanowire arrays, are desired to boost the bacterial catalytic performance. In this work, the physical interaction of *S. ovata* cells and vertical silicon nanowire arrays was investigated. When grown under conditions of increased ionic strength, *S. ovata* cells were found to undergo tuneable self-assembled parallel alignment with the nanowires. A Derjaguin-Landau-Verwey-Overbeek based model describing the kinetic and thermodynamic driving forces of bacteria-nanowire attachment is proposed. This insight into the nature of bacteria-nanostructure interactions has the potential to create artificially structured biofilms with not only improved catalytic performance, but induce new ensemble properties based on unnatural cell-substrate and cell-cell interactions, paving the way towards the next generation of nano-bio hybrid systems.

**COLL 573**

**Influence of nanoparticle coatings on environmental behavior and bioavailability: The role of transformations**

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Currently, there is an increasing body of research aimed at uptake and toxicity of nanomaterials in terrestrial ecological receptors; however, many studies fail to take into account biogeochemical transformations of nanomaterials that occur in natural and engineered environments such as in wastewater streams, during wastewater treatment, after introduction into natural soils and within organisms after their uptake or due to
interactions with organisms. This presentation will discuss how surface coatings are transformed in the environment and how these transformations impact binding to solid phases in natural soils as well as their bioavailability. The first focus is on how charge of polymer coatings influences binding of Ag and ZnO nanoparticles to soils and how this subsequently influences mobility in soil. The second focus is on how charge of polymer coatings on CeO₂ nanoparticles influences their bioavailability and how binding of natural organic matter to these surfaces influences bioavailability and toxicity in the nematode Caenorhabditis elegans. The results of these two studies demonstrated that while the charge and molar mass of Ag, CeO₂ and ZnO nanoparticle coatings has a profound influence on their environmental behavior, bioavailability and toxicity, this influence is rapidly lost in complex environmental media as the coatings are degraded or transformed. The final focus is on how nanomaterial bioavailability changes as a result of trophic transfer, presumably due to acquisition of a protein corona within organisms occupying different trophic positions. Studies in this area focus on Au nanomaterials and demonstrate how bioavailability is increased when nanomaterials are taken up through trophic transfer. Taken as a whole, these studies indicate that biogeochemical transformations need to be considered when investigating interactions between nanoparticles and environmental, biological or engineered surfaces.

COLL 574

Emergent properties of nanohybrids and their potential environmental implications

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Recent focus on material synthesis and development at the nano-scale shows a clear shift from single material processing toward hierarchical assemblages. Such ensembles of two or more pre-synthesized nanomaterials, known as nanohybrids (NHs), are primarily pursued to extract multifunctionality through alteration of their interfacial, electronic, and optical properties. NHs are already at use in commercialized energy, electronics, and medical products, which warrant immediate attention for safety evaluation. This talk focuses on NHs used as electrocatalysts in fuel cell technologies. Such electrocatalyst NHs are prepared with platinum (Pt), which is chemically reduced on niobium (Nb) doped semiconducting titania (TiNbOₓ) and distributed over multiwalled carbon nanotube (MWNT) surfaces. The TiNbOₓ-MWNTs are then characterized using STEM/EDX, TEM, and XRD. This talk will also present aggregation behavior and biological interaction of these NHs and their components. The electrocatalyst NHs show significantly enhanced colloidal stability compared to its component MWNTs. Also, the growth of fathead minnows is significantly reduced in presence of the NHs. Novel emergent properties (such as altered mechanical stiffness, electronegativity, and reactivity) are identified and measured and are correlated with their manifested
environmental behavior. This talk also highlights other emergent properties of NHs and proposes strategies to evaluate environmental implications of this ever-expanding set of nanomaterial.

**COLL 575**

**Engineering the optical properties of gold nanocubes by assembling into highly packed 2D arrays of different structure**

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Engineering the assembly of gold nanocubes, prepared by colloidal chemical technique, by arranging them into highly packed 2D arrays was found to improve their optical properties. The interparticle separation distance between the individual nanocubes in the 2D array was well-controlled by changing the chain length of the polymers bound to their surfaces. The organization of the nanocubes inside the 2D arrays was improved by using gold nanocubes fully covered with polymer. Discreet dipole approximation calculation made it possible to assign the experimentally measured localized surface plasmon resonance scattering spectrum of the 2D arrays. The multiple plasmon peaks are related to the plasmon field coupling between the fields of the individual nanocubes forming the 2D arrays. Interestingly, the intensity of the plasmon field was found to be high on the nanocubes locate in the center of the arrays for one plasmon mode while for other plasmon mode the field is high on the nanocubes locate in the terminal.

**COLL 576**

**Ab initio investigation of tribochemical phenomena in solid and boundary lubrication**

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Motor oils are usually enriched by chemical additives, which reduce friction and wear at microasperity contacts where hydrodynamic lubrication is no longer effective. In these conditions, known as boundary lubrication conditions, the additives react with the surfaces and modify their properties of adhesion, resistance to wear and friction. Recent experiments of gas phase lubrication, which have been carried out to understand the functionality of organophosphorus additives, revealed that a significant reduction of wear and friction at steel interfaces could be obtained by the tribologically-induced formation of iron-phosphide.[1] To get atomistic insight into this result, we performed an ab initio study of the mechanisms of iron phosphide formation from the dissociative adsorption of trimethylphosphite (TMPi) at the Fe(110) surface. We identify the reaction paths for P release at the surface by means of the nudged elastic band method and elucidated the effects of interfacial phosphorus on the properties of adhesion and resistance to sliding of iron interfaces. This latter analysis was performed for sulfur also,
which was found more effective in reducing adhesion and shear strength than phosphorus.

In the second part of the talk I will consider graphite and molybdenum disulphide (MoS2), which are well known solid lubricants. We performed density functional theory calculations, including van der Waals interactions, of interlayer adhesion and shear strength. We constructed the potential energy surfaces (PES), which governs interlayer sliding, and described its changes as a function of load. We found marked difference between the two materials and explained them analyzing the load-induced charge displacements.[2,3]


COLL 577

Tribofilms on real engine surfaces

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Surface active antiwear (AW) additives, such as zinc dialkyl dithiophosphate (ZDDP), are included in lubricant formulations to protect engine surfaces by building a thick, protective, oxide tribofilm. While many researchers have shown this formation mechanism in laboratory tests, few have shown data on parts taken from actual engine tests that would help prove the same mechanism occurs. Worn engine components are examined using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Fresh and used engine oil samples have also been tested in laboratory high-frequency reciprocating rig (HFRR) wear tests. Contrary to the popularly proposed mechanism, the engine components had no or little evidence of a classical thick tribofilm, even though they came from engine tests with little overall wear. The HFRR tests show that as the lubricant ages during engine operation, tribofilm forming ability decreases. We conclude that, though tribofilms may form and be protective, they are not always necessary for low friction and low wear. All evidence suggests that oxidation, which occurs naturally in an engine with time, reduces the ability of a formulation to form any tribofilm.

COLL 578

In-situ study of growth mechanisms and kinetics of ZDDP anti-wear tribofilms in nanoscale single-asperity contacts
Zinc dialkyldithiophosphates (ZDDPs) are lubricant additives used nearly universally in engine oils. Despite the generation of volatile phosphorous- and sulphur-containing compounds in the downstream gases that can reduce the working life of the catalytic converter, the unrivaled wear protection of ZDDPs makes them essential to the lubricant performance. ZDDPs work by decomposing under tribological sliding to form nanoscale anti-wear films whose growth mechanisms are still poorly understood due to the complexity of the macroscopic multi-asperity sliding interfaces and the multiple chemical species involved. Greater understanding of the formation of these films is essential to enable rational design of more environmentally-friendly and energy-efficient engine oil formulations. Here we report a novel experimental approach using atomic force microscopy (AFM) for visualizing and quantifying the formation of ZDDP anti-wear films in-situ in a single asperity contact with nanometer-scale spatial resolution. Experiments performed on iron-coated silicon surfaces at 80-140 °C in the presence of ZDDP containing polyalphaolefin oil show that thermal films grow on the substrate in the absence of tribological contact. These films are easily removed by sliding the tip at applied normal forces of only a few nanonewtons (contact pressure < 1.0 GPa). Continued sliding at higher normal loads (contact pressure ~ 2.0 - 6.0 GPa) reveals the nucleation and growth of much more robust films with a pad-like lateral structure, similar to their morphology in macroscopic contacts. The growth rate is nonlinear with time, and increases exponentially with temperature and contact pressure, in agreement with the reaction rate theory. This is the first direct confirmation and quantification of asperity-level formation of ZDDP-derived anti-wear films, enabling us to directly compare with atomistic predictions and other possible proposed mechanisms.

COLL 579

Shear-induced chemical reaction pathways on copper

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The formation of a boundary film by reaction with a gas-phase lubricants or lubricant additives formally occurs in several steps that involve the initial adsorption and reaction of the lubricant molecule on the surface, followed by shear-induced decomposition and
formation of the boundary film. Fully understanding this sequence of reaction steps will enable the structure of the additive molecule to be related to the nature of the resulting boundary lubricating film.

The approach is illustrated using the gas-phase lubrication of copper by dimethyl disulfide (DMDS). DMDS initially reacts with copper at $\sim 300 \, \text{K}$ to form thiolate species and shear at the interface causes sulfur and some carbon to penetrate the substrate to form a boundary film that reduces friction. The kinetics of the shear-induced rate of thiolate decomposition is measured in ultrahigh vacuum from the amount of methane that is formed as the surfaces rub, where the reaction rate increases by about six orders of magnitude compared to the thermal decomposition rate. Models for the increase in shear-induced decomposition rate will be discussed.

**COLL 580**

**Mechanochemical activation of zinc dialkyl dithiophosphate**

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Zinc dialkyl dithiophosphate (ZDDP) is routinely used as an antiwear additive in engine lubricants and is activated by heat and rubbing experienced in tribological contacts\([i]\). In the contact ZDDP forms a protective tribofilm which can be more than 100 nanometers thick. Many other mechanically activated reactions have been studied using classical mechanochemical methods\([ii]\) but have not been compared to the tribochemistry of ZDDP. This study investigates the relationship between ZDDP tribochemistry in a lubricated contact and the mechanochemistry of ZDDP in a traditional ball mill grinder to determine the role of mechanical activation on ZDDP reactivity and wear protection. ZDDP was shaken at room temperature under typical mechanochemical reaction conditions in a mechanical ball mill. The intermittent mechanical contact in a ball mill is significantly different than the continuous frictional sliding and rolling contact encountered in a lubricant wear experiment. Analysis by x-ray photoelectron spectroscopy (XPS), auger emission spectroscopy (AES) and infrared spectromicroscopy demonstrate that under traditional mechanochemical conditions ZDDP is reactive and undergoes a chemical transformation. ZDDP reaction product produced in the ball mill is chemically related to the composition of the tribofilm formed in lubricant wear tests. These results suggest that ZDDP antiwear activity can be understood in terms of classical mechanochemical reaction chemistry.


COLL 581

Photo-chemical reactions on plasmonic metal nanostructures

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We will show that composite photo-catalysts combing plasmonic metallic nanoparticles of noble metals and semiconductor nanostructures exhibit improved photo-chemical activity compared to conventional photo-catalytic materials.1,2 We will also show that plasmonic silver nanoparticles, optically excited with low intensity visible light, exhibit direct photo-catalytic activity. We will discuss underlying mechanisms associated with these phenomena.2,3,4 We propose that this new family of photo-catalysts could prove useful for many heterogeneous catalytic processes that cannot be activated using conventional thermal processes on metals or photo-catalytic processes on semiconductors. I will show an example of such a process.5

1. D. B. Ingram, S. Linic, JACS, 133, 5202, 2011

COLL 582

Visualization of compression and spillover in a coadsorbed system: Syngas on cobalt nanoparticles

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The development of sustainable energy technologies, including green fuels, is of global importance. In this respect, Fischer-Tropsch synthesis (FTS) has recently gained attention, as it involves the formation of fuels via the reaction of syngas (carbon monoxide and hydrogen), which can be derived from renewable sources. FTS often employs cobalt-based nanoparticle catalysts that are greatly affected by the state of reactants, as well as the catalyst's shape and size. Nanoscale investigation of model cobalt catalysts can elucidate important information about the reactants, which can guide catalyst improvement and lower the cost of FTS-derived fuels. To this end, scanning tunneling microscopy was used to study the interaction of syngas with model cobalt nanoparticles on copper. It was found that hydrogen and carbon monoxide form segregated islands on the nanoparticle surfaces, and excess carbon monoxide compresses and displaces the hydrogen islands. Compression is known to affect selectivity and reactivity in a number of important industrial reactions; this nanoparticle system allows for visualization of how compression affects FTS reactants. These results may have significant ramifications in the reaction rate of FTS on cobalt, as the
segregation of carbon monoxide and hydrogen, as well as the displacement of hydrogen by carbon monoxide, limits the reaction interface.

**COLL 583**

**Spatiotemporal catalytic dynamics within single nanocatalysts**

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This presentation will describe our work of using single-molecule fluorescence microscopy to interrogate spatial and temporal correlations of catalytic reactions on single nanocatalysts and with single crystal facets at single-reaction resolution and nanometer precision. We have imaged and resolved catalytic reactions on a single shaped 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, and show that catalytic reactions can “communicate” with each other over a distance of hundreds of nanometers and a timescale of tens to hundreds of seconds within a single nanocatalyst. This catalytic communication is phenomenologically analogous to allosteric effects in enzymes, nature's most important catalysts.

**COLL 584**

**Visualizing metal-hydride nanoparticle phase transitions with nanometer-scale resolution**

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Many energy and information storage processes, such as battery charging, hydrogen storage and memory switching, rely on phase changes of nanostructured materials in reactive environments. Compared to their bulk counterparts, nanostructured materials appear to exhibit faster charging and discharging kinetics, an extended life cycle, and size-tunable thermodynamics. However, in ensemble studies of these materials, it is often difficult to discriminate between intrinsic size-dependent properties and effects due to sample size and shape dispersity. Here, we present the first direct measurement of hydrogen absorption and desorption in individual palladium nanocrystals, with sizes ranging from 29 nm down to 13 nm. Our approach is based on in-situ electron energy-loss spectroscopy (EELS) in an environmental transmission electron microscope. By constructing single-particle pressure - energy-loss isotherms, we find that hydrogen intercalation in Pd nanocrystals is regulated by the coherent elastic coupling between the alpha and beta phases of PdHₓ. Such coupling results in an energy barrier that cannot be overcome by thermal fluctuations, suppressing coexistence of alpha and beta phases. Consequently, hydrogen loading and unloading isotherms are characterized by
abrupt phase transitions and macroscopic hysteresis gaps. These findings are in striking contrast with conventional first-order phase transitions, and also deviate from ensemble measurements of Pd nanoparticles, which have suggested a thermally-driven nucleation of the hydride phase. Furthermore, we find that surface energy plays a critical role in determining the energetics of the hydrogen absorption process. Our results provide a general framework for monitoring phase transitions in individual nanocrystals in a reactive environment and highlight the importance of single-particle approaches to the characterization of nanostructured materials.

COLL 585

Catalysis at the interface of nanocrystals

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Recent developments in nano-science have opened up new directions in chemistry to allow the synthesis of new nano-materials which could not be obtained by conventional means. The current research shows that they exhibit many fascinating size and shape dependent properties. The use of well-defined, well-characterized pre-formed nanomaterials as building blocks for the synthesis of functional materials with controlled interface is a new direction for many exciting applications. In this meeting, novel nanoparticles of controllable composition, size, morphology, surface and interface will be presented. Some of them show exceptional catalytic activity and selectivity towards desired products. Typically, we will show that by employing nanotechnology, nano-materials with tailored sizes decorated with foreign atoms in a controlled manner in colloid solution as preformed nanocatalysts can be tuned to give high activity, whilst the undesirable reactions can be suppressed. This is achieved through blockage of unselective low coordination sites and the optimisation in electronic influence of the nanoparticle of appropriate size by the decoration. This work clearly demonstrates the advantage in engineering preformed nanoparticles via a bottom-up construction and illustrates that this route of catalyst design may lead to improved catalytic processes.

COLL 586

Computational design of bio-inspired hybrid soft biomaterials

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Our objective is to design hybrid biomaterials through the self-assembly of different representative amphiphilic molecular species present in biological cell membranes. Individual molecular species are represented by a hydrophilic head group and two hydrophobic tails. The species can differ in terms of specific chemical properties of the polar head groups and the hydrocarbon tail groups. The amphiphilic molecules form a
stable hybrid vesicle via the self-assembly in the presence of a hydrophilic solvent due to their amphiphilic nature. We use a Molecular Dynamics-based mesoscopic simulation technique called Dissipative Particle Dynamics to simultaneously resolve the aggregation dynamics, structure and morphology of the hybrid aggregate. In addition, we investigate the factors that control the self-organization of the molecular species within the hybrid soft biomaterials. The results of our investigations can be used for the design and prediction of novel hybrid soft materials.

**COLL 587**

**Visible Mie scattering from hollow silica particles with particulate shells**

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A series of core/shell polystyrene/silica colloidal nanocomposite particles are synthesized by alcoholic dispersion polymerization of styrene in the presence of an ultrafine alcoholic silica sol. Hollow silica shells are formed on calcination of the polystyrene cores, as confirmed by TEM studies. On visual inspection in transmittance mode (illuminated background), the dry silica powders appear yellow to red in color, but when viewed in reflectance (dark background) relatively intense blue/green colors are observed. The latter phenomenon has been analyzed by visible reflectance spectroscopy and the reflectance maximum depends on the dimensions of the silica shell, which are in turn dictated by the initial nanocomposite particle diameter. SAXS is used to determine the packing density of the silica nanoparticles within the silica shell in both the original polystyrene/silica nanocomposite particles and also in the calcined silica shells. Combined with geometrical considerations, this allows the equivalent uniform silica shell thickness to be calculated for a particulate fused silica shell and related to recent theoretical predictions for hollow particles comprising uniform contiguous silica shells.

**COLL 588**

**Characterization of a core-shell hybrid nanostructure using field-flow fractionation, electron microscopy, and single-particle ICP-MS**

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A methodology has been developed to measure mass, size and density of the core and the shell of a core-shell nanoparticle for the first time.

The FFF-based methodology allows for the measurement of the mass of the nanoparticle using Centrifugal Field-Flow Fractionation (CFFF) and the volume by Asymmetrical Flow Field-Flow Fractionation (AsFIFFF). The nanoparticle density can then be calculated from the obtained mass and volume data. Mass of the core can be
measured either by Single-Particle ICP-MS or by the FFF analysis of the uncoated core nanoparticle. The measured nanoparticle size was confirmed by Dynamic Light Scattering and electron microscopy.

The methodology was validated by measuring the density of different sized polystyrene latex beads standards. The measured densities of the polystyrene standards were in the range of 1.04 g/mL to 1.05 g/mL

Data will be presented for the analysis of a silver-shelled gold nanoparticle standard. The diameter of the nanoparticle was measured as 56 nm with core diameter and shell thickness of 30 nm and 13 nm respectively. The mass of the nanoparticle was measured as $0.876 \times 10^{-15}$ g with a shell to core mass ratio of 3.5.

The densities of the core, shell and core-shell nanoparticle were measured as 12.8 g/mL, 8.9 g/mL, and 9.5 g/mL respectively.

The data suggests a 33% porosity in the gold core and a 16% porosity in the silver shell.

**COLL 589**

**Electrospun hybrid fibers composed of poly(ε-caprolactone) and polyhedral oligomeric silsesquioxane-based copolymer**

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Polyhedral oligomeric silsesquioxane (POSS) nanocages have been investigated for many applications in past years, but their uses in block copolymers for electrospun materials remains a relatively unexplored research area. With poly[(propylmethacryl-heptaisobutyl-polyhedral oligomeric silsesquioxane)-co-(methylmethacrylate)] (POSS-MMA)/poly(ε-caprolactone) (PCL) blends being used as the model system, this is a study of the morphological and structural features of uniform POSS-MMA/PCL hybrid composite fibers prepared by single-nozzle electrospinning. This study provides detailed insight into the encapsulation capacity of POSS-MMA as a shell material for the electrospinning of core/shell fibers. The bicontinuity of hybrid core/shell fibers can be tuned by controlling the phase separation of POSS-MMA/PCL in electrospinning solutions and therefore the size of PCL-in-POSS-MMA emulsion droplets. Our results demonstrate the enhanced encapsulation capacity of POSS-MMA copolymers as shell materials. Taking advantage of the rapid advancement of POSS-based polymer synthesis, this study can potentially be generalized to guide the fabrication of various other POSS-based core/shell nano/microstructures by using single-nozzle electrospinning or coaxial electrospinning.
Complex architecture of electrospun organic-inorganic hybrid fibers

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Morphology and complex internal structure of electrospun poly(e-caprolactone) (PCL)/PSS-(1-propylmethacrylate)-heptaisobutyl substituted (POSS) hybrid fibers were examined in this study. Scanning electron microscopy revealed nanopapillae and wrinkles on the surface of the PCL/POSS hybrid fibers. The combination of morphological and surface analyses suggested that the wrinkles were mainly composed of POSS, while the PCL-rich phase was mainly located in the core of the fibers. Two-dimensional wide-angle X-ray diffraction studies demonstrated that the chain axis of PCL crystallites aligned parallel to the long axis of the fibers, and the POSS interlocked in the amorphous regions of PCL along the fiber axis. Water droplet evaporation profiles were also discussed in relation to both the surface chemical compositions and the secondary surface nanostructures of the hybrid fibers. The evaporation dynamics of water droplets placed on the PCL/POSS fibers were fundamentally different from those placed on neat PCL fibers.

Hybrid nano building blocks for pixelated EUV photoresists and dielectric thin-films

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In this research program we are synthesizing and characterizing a set of macromolecular materials, Nano-Building Blocks (NBBs) with ~1 nm³ volume, capable of serving as “pixelated” photoresists for the next generation of photolithography. Specifically, we are producing silsesquioxane and polyoxometalate cored NBBs for thin-films and evaluating film-forming capabilities, EUV patterning, and dielectric properties for semiconductor industry applications. Each potential NBB possesses multiple functional vertices and high thermal stability. Of significant interest is the polyoxometalate core, composed of high atomic number metal atoms, which show a relatively high absorption of 13.5 and 6.7 nm photons.

The flexibility of the silsesquioxane and polyoxometalate-imide chemistry is well suited to this project, allowing for the grafting of a wide variety of organic functionality to the discrete inorganic core. The functionality explored here is polymerizable, however future opportunities exist to incorporate optical and ion-transport functionality.
With these capabilities, hybrid NBBs present the opportunity to produce novel materials and study the resulting nanoscale behavior. One potential use is the development of pixelated, non-chemically amplified, extreme ultraviolet (EUV) photoresists, while additional opportunities include low and high-k dielectric thin-films and radiation hardening. Opportunities in tuning dielectric response are expected by manipulating the connectivity between adjacent NBBs and mixing NBBs.

The result of this work will be a scalable and flexible NBB platform for EUV photoresists and photo-curable, tunable, dielectric films for the next generations of semiconductor devices with opportunities in a wide variety of thin-film applications. This platform will be characterized by its use of scalable syntheses presenting extreme flexibility in order to adapt to processing requirement in the EUV regime.

**COLL 592**

**Transparent and hard zirconia-based hybrid film with multiple functions**

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A Transparent and Hard Zirconia-based Hybrid Film With Multiple Functions

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A transparent and hard zirconia-based hybrid film multiple functions, such as exceptional dynamic/thermo-responsive oleophobicity, thermal durability, reasonable hydrolytic stability, and anti-fingerprint properties was successfully fabricated by a simple spin-coating method through a combination of zirconium (Zr) tetra-propoxide with a branched-stearic acid (BSA). The effect of decreasing the BSA content \( n \) from \( n = 1 \) to \( n = 0.1 \) was investigated and found to significantly alter the oleophobic properties of the Zr:BSA films. Poor oleophobic dewettability was observed when \( n = 1 – 0.6 \), however drastic improvement in contact angle hysteresis and minimum required tilt angles was measured for \( n \leq 0.5 \). This shift in surface interaction was attributed to a change in the physical nature of the surface-tethered BSA, from tightly packed “solid-like” arrays in \( n > 0.5 \) hybrid films, to an arrangement in which the functional groups possessed adequate space to move and behave in a liquid-like manner. The increased liquid-like surface properties created using this approach are thought to reduce the resistance to motion of liquid droplets, allowing easier dewetting of low surface tension alkane liquids. In addition, thanks to the thermal stability of BSA, our Zr:BSA hybrid films displayed a greatly improved thermal effective range (maximum 200 °C).

Nanoindentation confirmed that the hardness of the Zr:BSA hybrid films were markedly
increased by curing at 200 °C for 1 h (from 1.95 to 3.03 GPa), whilst dynamic
dewettability toward \(n\)-hexadecane was maintained. Small volume \(n\)-hexadecane
droplets (5 μL) were easily set in motion, sliding across and off our best Zr:BSA hybrid
film surfaces at low tilt angles (< 10°) without pinning. Moreover, they also showed
thermoreponsive dynamic dewetting behavior and reasonable resistance to hydrolysis
in an aqueous environment.

References


COLL 593

Preparation and characterization of phase change material and fragrance
microcapsules

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Microencapsulation technology has found a variety of applications in many areas such
as pharmaceuticals, cosmetics, textiles, agriculture, and etc. Here we developed a
novel microcapsule for encapsulation of phase change material and fragrance.

The mixture of octadecane as phase change material and dementhonized peppermint oil
as fragrance was encapsulated by polyurea (PU) through interfacial polymerization of
Isophorone diisocyanate (IPDI) and hexamethylenediamine (HMDA). Morphology and
chemical structure of PU microcapsules were characterized by optical microscopy,
scanning electron microscope (SEM) and FTIR. The thermal properties of
microcapsules were studied by differential scanning calorimetry (DSC) and
thermogravimetric analysis (TGA). Results show that the resulting PU microcapsules
are spherical and rough. The mean size of PU microcapsules is about 7.0 μm and high
latent heat storage density is 169.1 J/g. PU microcapsules exhibited a good thermal
stability under 200°C. PU microcapsules encapsulating octadecane and dementhonized
peppermint oil will find applications such as textile and garment, building materials,
heat-transfer fluid and so on.

COLL 594

Distance and plasmon wavelength dependent fluorescence of molecules bound
to silica-coated gold nanorods: A study of plasmon-induced luminescence
enhancement

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Plasmonic nanoparticles can strongly interact with adjacent fluorophores resulting in plasmon-enhanced fluorescence or fluorescence quenching. Dipolar coupling is dependent upon the composition of the nanoparticle, distance between the fluorophore and the plasmonic surface, the transition dipole orientation and the fluorophore’s absorbance/emission wavelengths relative to the surface plasmon band of the nanoparticles.

In this work, we examine the distance and plasmon wavelength dependent fluorescence of IRDye 800CW DBCO bound to gold nanorods. Nanorods with plasmon bands ranging from 530 – 850 nm are synthesized and coated with mesoporous silica shells 11 – 26 nm thick. IRDye is covalently attached to the silica surface via copper-free click chemistry. Using time-resolved techniques, a strong reduction in fluorescence lifetime is observed with decreasing silica shell thickness and when the plasmon band is closer to IRDye absorption/emission, with no loss in emission intensity. Steady-state measurements also demonstrate wavelength and distance dependent emission. Maximum fluorescence intensity with a 10 fold enhancement is observed with 17 nm silica shells when the gold nanorod plasmon band is resonant with IRDye absorption.

In addition, control experiments are carried out to confirm that the observed changes in fluorescence are due to plasmonic interactions, not simply attachment to a silica surface. There is no change in fluorescence lifetime or steady-state intensity when IRDye is bound to mesoporous silica nanoparticles. In addition, IRDye loading is limited to maintain a distance between dye molecules on the surface to more than 9 nm, well above the Förster radius. This assures minimal dye-dye interactions on the surface of the nanoparticles.

**COLL 595**

**Large-scale silica overcoating of gold nanorods with tunable shell thicknesses**

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Gold nanorods (GNRs) with SiO$_2$ overcoatings are of interest for enhancing the stability of GNRs during photothermal heating, for allowing functionalization with silanes, and for some specific applications, such as ultrasound imaging. While methods have recently been developed for synthesizing GNRs on a large scale, SiO$_2$ overcoating reactions are still limited to small reaction scales. Here, we report a method for large-scale overcoatings, which gives $\sim$200 mg of SiO$_2$-overcoated GNRs (SiO$_2$-GNRs). SiO$_2$ overcoatings are deposited onto and encapsulate the cetyltrimethylammonium bromide (CTAB) bilayers that stabilize GNRs by continuously adding tetraethoxysilane (TEOS) via syringe pump. Continuous addition is important for keeping the TEOS concentration sufficiently low to allow for uniform overcoatings on individual GNRs. Optical
absorbance spectra of SiO$_2$-GNRs closely resemble uncoated GNRs, which indicates overcoating of single (rather than multiple) GNRs and confirms that they remain well dispersed. The SiO$_2$ shell thickness can be controlled by adjusting the reaction conditions, giving shells as thick as 30 nm. For thin (< 10 nm) coatings, addition of a poly(ethylene oxide) silane (PEG-silane) during growth allows for facile control over the shell thickness, giving overcoatings as thin as 3 nm. The bulky PEG chain terminates further crosslinking and deposition of SiO$_2$; timing of addition of PEG-silane allows for control of the SiO$_2$ shell thickness.

**COLL 596**

**Gold nanorods in the extracellular matrix and their effect on cancer cell migration**

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Gold nanorods are widely studied for biological applications for imaging, drug and gene delivery, and photothermal therapy of cancer. In order to utilize these nanomaterials safely in the human body, it is imperative to investigate additional interactions between gold nanorods and cells. Few studies look at how these nanoparticles may affect cellular interactions with their three-dimensional surroundings. Nanoparticles in the body would not only come into contact with cells, but with extracellular matrix (ECM) proteins and secreted soluble proteins.

We have mimicked the ECM of human breast cancer cells with three-dimensional collagen cell cultures. Nested gel matrices have allowed us to explore the effect of nanorods dispersed in the matrix on metastatic breast cancer cell migration. It was observed that gold nanorods in the ECM increase spontaneous cell migration. The mechanism behind this change in cell behavior is hypothesized to be due to differences in mechanical properties, diffusion of soluble factors, or physical blocking of cell-collagen interactions. We have examined the mechanics and structure of the gels themselves via rheology, confocal reflectance and scanning electron microscopy, and the diffusion of molecules via fluorescence recovery after photobleaching techniques. We have also looked for changes in cell morphology with brightfield and confocal fluorescence microscopy, the mechanism of movement with time-lapse microscopy and monitored the expression of matrix metalloproteinases and proteins involved in cell migration.

**COLL 597**

**Insights on the microscopic mechanisms of anisotropic growth of gold nanorods from molecular dynamics simulations**

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Gold nanorods are widely used in many areas such as photothermal cancer therapy, biochemical sensing and medical imaging due to their size and shape dependent optical properties [1]. Directly manipulating and controlling the size and shape of metal nanoparticles is therefore a key step for their tailored application. Gold nanorods are normally prepared using seed-mediated growth technique, which require gold seeds, ascorbic acid and aqueous cetyltrimethylammonium bromide (CTAB) solution of HAuCl₄. Isotropic morphology breaking of the seeds by crystal twinning results into formation of pentatetrahedral nanorod structure with different facets. Although possible mechanism have been proposed, the microscopic understanding of the anisotropic growth is still missing.

We use molecular dynamics simulations in order to understand the microscopic origin of the asymmetric growth mechanism in gold nanorods. We provide the first atomistic model of adsorption of CTAB on different surfaces, namely (111), (110) and (100) in growing electrolyte solution. We find that on all the investigated surfaces, the CTAB form a layer of distorted cylindrical micelles where channels among micelles would provide direct ions access to the surface. In particular, we show how AuCl₂⁻ ions, can freely diffuse from the bulk solution to the gold surface. We also find that the (111) surface exhibits the higher CTAB packing density and the higher electrostatic potential. Both elements would favor the growth of the nanorod in the direction of (111) facet [2].

Furthermore, we investigate the effect of halide ions (X= Cl⁻, Br⁻ and I⁻) on adsorption of CTAX on the (111) surface and we provide a rational for the influence of halide ions on anisotropy of gold nanoparticles.


Fabrication of Au-coated Pt nanoframes via chemical etching and regrowth

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The synthesis of optically active nanostructures attracts researchers' interests due to their unique optical properties. Au and Ag nanostructures effectively interact with the light at the specific wavelength depending on their shapes. In terms of synthesizing Au nanoframes, most researchers select the galvanic replacement reaction on Ag nanoplates, but the structural weakness of thin Au ring easily induces aggregates.

In my presentation, I will introduce an effective synthetic strategy to produce Au-coated Pt (Pt@Au) nanoframes. The Pt nanoring at the inner core acts as a framework, and Au coated on the Pt nanoring allows the nanosstructure to behave optically active as pure Au nanoframes because of the surface plasmon coupling between Au and Pt. This research provides fundamental basis in order to understand the optical property of Au nanoframes.

The experimental process consists of two regimes, etching and regrowth process. We adopt site-selective grown Au@Pt nanoplates as a seed, in which Pt selectively grow along the edge of Au nanoplates. We took advantage of rim-preferential growth synthetic method to finally synthesize Au nanorings, through etching and regrowth processes.

Au$^{3+}$ ions in growth solution play a critical role as both of an etchant and a metal precursor. In the etching process, as Au plates at the central part is selectively etched out by Au$^{3+}$ ions in absence of reductant, leaving only Pt rims. Pt-dominant nanorings are remained at the end of reaction. By adding ascorbic acid, a reducing agent, it initiates the regrowth of Au on Pt nanoring by reducing Au$^{3+}$ ions present in the growth solution. The resultant product is in the form of Au-coated Pt nanoframes, which take advantage of the empty space among the nanoparticle, providing relatively high light transparency and reactant permeability in nano-optics and catalysis.

Theoretical description of architectures of gold nanoparticles

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Density Functional Theory simulations including dispersion provide a detailed atomistic model for understanding of synthesis-structure relationships in the study of material
sciences and catalysis.1 We have investigated the role of different compounds in the synthesis of gold-nanorods to identify key of the leading interactions that drive the formation of Au nanorods.2 The complexity of the procedure can be analyzed in detail and the information provided by the calculations paves the way for a better compression of the structure of this novel family of materials.

The resulting insights significantly advance the state-of-the-art to improve our knowledge of the roles and effects of electrostatic and van der Waals interactions, opening a complete new perspective in the control of new architectures to design of the nanoparticles.3


COLL 600

Gold nanorod synthesis: A multivariate factorial design of experiments

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Since discovery of the seed-mediate synthesis of gold nanorods around the beginning of the 21st century, progress in improving the yield of gold nanorods has been arduous at best. Furthermore, some synthetic control has been found through traces amounts of silver nitrate; however, the process has difficulties with reproducibility, monodispersity, and morphological impurities. Multivariate factorial design of experiments allows for the measurement of multiple effects and their addition with more precision and fewer trial runs than one-factor-at-a-time design of experiments. Multivariate factorial design of experiments detects and measures non-additive, interaction effects (i.e. coupled & higher-ordered factor interactions); whereas, one-factor-at-a-time design of experiments is restricted to studying one variable while holding all other factors fixed. Here in, we present a factorial design of experiments of seed-mediated synthesis of gold nanorods simultaneously considering numerous factors including the amount of NaBH₄, gold seed particles, ascorbic acid, silver nitrate; the age of the seed solution; the temperature of the synthesis; and many more. The effect of these variables on the longitudinal localized surface plasmon resonance peak position; absolute nanoparticle dimensions, distribution, and morphological impurities; and total Au⁰ yield were monitored to determine important design factors in controlling these features of the product gold nanorods.

COLL 601

Enhanced catalytic activity of bimetallic silver/gold mixed metal-oxide nanocomposite materials

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We synthesized silver/gold (Ag/Au) alloy nanoparticles via the galvanic replacement reaction between maltose coated Ag nanoparticle (Ag NP) seeds and tetrachloroauric acid. This synthesis method is facile, economic, and environmentally benign. Nanoparticle catalytic activity was evaluated using the reduction of para–nitrophenol by sodium borohydride as a model reaction. Catalytic activity was enhanced 5-fold relative to pure Au and Ag. These bimetallic NPs (Ag/Au) were then immobilized on (TiO₂, FeTiO₃) nanomesh structures and tested using the para–nitrophenol model reaction described above. We also evaluated the photocatalytic activity of these nanocomposites against rhodamine B using broadband visible and laser (532 nm) irradiation. The photocatalytic efficiency was optimized by adjusting the size, shape and composition of the nanoparticles to generate new functionalities not exhibited by these individual nanostructures. Moreover, immobilization of bimetallic NPs (Ag/Au) within nanomesh structures alleviates the inherent challenges of nanoparticle aggregation and rapid
dissipation in aqueous environments. The present study provides critical mechanistic insights to the growing research field of photo-assisted, nanocomposite-based remediation.

**COLL 602**

**Fabrication of shape-controlled graphene nanoring arrays using Au@Pt nanoplate lithography methods**

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Various nano-sized graphene shapes such as graphene nanoribbons and graphene nanomesheshave gained a great deal of attention for electronic device applications. Here, we fabricated a variety of graphene nanoring arrays using various Au@Pt ring-shaped nanoplates as a pattern mask. Amorphous graphene nanoflakes that were prepared by chemical reduction of graphene oxide are assembled into a 2-dimensional assembly at the water/oil interface, and then various shapes of Au@Pt nanoplates were utilized as a pattern mask in order to convert the amorphous shape of graphene into circular, triangular, and hexagonal graphene nanorings. Shape-controlled graphene nanorings were analyzed using SEM, XPS, AFM and Raman spectroscopy.

**COLL 603**

**Two-photon absorption enhancement of dye-modified gold nanorods studied by gain modulation**

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Two-photon absorption (TPA) has potential applications in three-dimensional imaging, nanosculpting and photodynamic therapy. However, meager TPA cross-sections limit the utility of TPA as a technology. Previous studies in our group and others indicate the ability of using the strong electric fields of plasmonic particles such as gold nanorods to enhance effective TPA cross-sections. In this work, we use a modified pump-probe technique based on gain, i.e., stimulated emission modulation, to determine two-photon properties. We study the distance-dependent two-photon cross-section enhancement of a designer TPA chromophore on gold nanorods with polymer spacer layers.
CO oxidation on supported noble metal catalysts: Insights from DFT study

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Distinctions between supported Au and Pt catalysts on TiO$_2$(110) for CO oxidation have been investigated by means of density functional theory calculations. Our study shows that the following factors determine the obvious differences between two kinds of catalysts for CO oxidation: (1) The adsorption strength of Au$_{11}$ is much weaker than that of Pt$_{11}$ on TiO$_2$(110), but both are strongly dependent on the surface properties of TiO$_2$. The addition of Pt increases the interaction between the alloyed cluster and TiO$_2$ support. (2) O$_2$ can adsorb only on the interfacial site between Au and TiO$_2$(110), whereas O$_2$ can adsorb on both the interfacial and metal sites of supported Pt nanoparticles. (3) CO is directly activated by the adsorbed molecular oxygen on the interfacial site of Au$_{11}$/TiO$_2$(110)$_{OH}$. While on Pt$_{11}$/TiO$_2$(110)$_{OH}$, the main reaction pathway is the dissociated oxygen reacting with CO. Once a Pt ensemble is formed on Au clusters (such as Au$_8$Pt$_3$/TiO$_2$(110)$_{OH}$), both of the reaction mechanisms work.

Manipulation of bacteria with free or immobilized nanoparticles: What a difference the surface makes

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A longstanding goal for the development of sensors or specialized materials is the ability to adhesively capture bacteria, kill them, and release them later. “Antimicrobial materials” that are completely non-adhesive to bacteria are inappropriate for sensors and those which release antimicrobial compounds have the disadvantage of toxicity and ultimate depletion of compound. Using nanoparticles as the active agent, we developed surfaces with controlled bacterial adhesion, killing, and release functionality. This talk demonstrates how using nanoparticle to cluster adhesive functionality leads to tuned bacterial adhesion, and limits bacterial evolution on the surface, facilitating bacterial release. The program also explores the bacteriocidal character of the surfaces. The substantially greater killing effectiveness of nanoparticles on a surface compared with free in solution further argues that classical mechanism are not a factor on these surfaces.

Ordered peptides and proteins at interfaces
Molecular structures of peptides and proteins at interfaces were examined using sum frequency generation vibrational spectroscopy, supplemented by a variety of other analytical techniques. Interactions between various model cell membranes and peptides including antimicrobial and cell penetrating peptides as well as proteins such as G proteins and G protein coupled receptors were studied in situ in real time. Surface immobilized antimicrobial peptides and enzymes were also studied and their structures were deduced. Such structural information was successfully correlated to their function and activity. It was found that peptides and proteins at interfaces are ordered, and their structures mediate their functions and their interactions with bacteria and cells.

**COLL 607**

Super-repellent antimicrobial surfaces

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We prepared hierarchically structured, superhydrophobic surfaces with dual- and triple-scale roughness via a layer-by-layer (LbL) particle deposition approach. The triple-scale structure was especially effective in achieving low roll-off angles for small water droplets, and demonstrated much higher stability for the non-wetting Cassie state over the dual-scale structure, as experimentally verified by a compression test. The dual-/triple-scale structured, superhydrophobic surfaces exhibited significantly reduced protein adsorption (up to 90% decrease). Platelet adhesion and activation was completely suppressed on the triple-scale structured surface. The hierarchically structured surfaces were further rendered antimicrobial by covalently incorporating bacteria-killing moieties onto the surface.

**COLL 608**

Comparison of peptide structure-lipid bilayer interactions for alamethicin, chrysophsin-3, indolicidin, and SMAP-29: Differentiation through QCM-D signatures

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Many antimicrobial peptides (AMPs) are thought to kill bacteria by attaching to cell membranes and disrupting the lipid bilayer structure. They act either by creating stable pores through which ions and molecules may travel or by destroying the membrane
through lipid removal. Although many studies have confirmed the pore formation and membrane lysis caused by the AMPs, the direct relationship between AMP structural characteristics and its mechanism of membrane interaction are not yet well understood. In this study, we have used quartz crystal microbalance with dissipation monitoring (QCM-D) to probe the interactions between a phosphatidylcholine (PC) supported bilayer membrane and the four peptides: alamethicin, chrysophsin-3, indolicidin, and sheep myeloid antimicrobial peptide (SMAP-29), with the goal of identifying QCM-D signatures that clearly differentiate the mechanism of action of these peptides. Multiple signatures from the QCM-D measurements were extracted that provided information on peptide addition to and lipid removal from the membrane, the dynamics of their interactions and the rates at which the peptide actions are initiated. The QCM-D signatures were interpreted in terms of molecular processes including pore formation, surface adsorption of peptide, and the insertion of the peptide or peptide aggregate into the bilayer. We found that the membrane interactions of each peptide involved a different sequence of molecular processes. These mechanistic variations in peptide action were related to the fundamental structural properties of the peptides including the number of amino acids, net charge, hydrophobicity, hydrophobic moment, accessible surface area and the probability of α-helical secondary structures. The study demonstrates that QCM-D provides a rich collection of unique signatures capable of differentiating the detailed mechanism of action of antimicrobial peptides.

COLL 609

Exploring structure/function relationships of bacterial lipopolysaccharides and lipid A with man-made surfaces presenting antimicrobial peptides

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For prokaryotic organisms like bacteria, their interaction with their environment is dominated by the constituent molecules of their outer cell walls or membranes. The physiochemical properties of these molecules influence how the cells respond to environmental conditions, such as temperature, pH, and salinity (ionic strength), but also how they interact with surfaces. For Gram negative bacteria, such as Escherichia coli and Yersinia pestis, these molecules are the lipopolysaccharides, found at the outer membrane. These molecules consist of, for most species and serotypes, a 10-50 heterogeneous chain of polysaccharides anchored to an amphiphilic lipid A core, which embeds it into the inner cell membrane. Lipid A, with a mostly conserved chemical structure amongst bacterial species, is of particular importance because it the cause of sepsis. We have investigated the structure/function relationship of LPS and lipid A molecules isolated from Yersinia pestis grown under different environmental conditions.
towards binding to a small set of immobilized antimicrobial peptides. Using surface plasmon resonance light scattering experiments, we have observed the effects of different LPS and lipid A chemical structures in different environments on both binding to the peptide derived surfaces as well as the aggregation behavior. Developing a greater fundamental understanding of the interfacial behavior of LPS and lipid A is paramount for applications such as biosensors and bio-resistant surfaces.

COLL 610

Protein behaviour in biomimetic nanoscopic environment

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The study of protein stability and bioactivity within a confined space has important ramifications across several areas ranging from protein therapeutics to food industry. The long-term stability and targeted delivery of proteins is still an elusive goal. Proteins have been usually studied in diluted solution or as single protein not allowing to understand the important effect of protein-protein interaction. This lead to study the effect of volume exclusion by one soluble macromolecule on another ('macromolecular crowding'), as well as assessing the effect of volume exclusion on a soluble macromolecule ('macromolecular confinement'). While in the last few years several studies provide interesting insights regarding protein dynamics, they are often limited by the strong interaction between the confinement/crowding agent and the protein. In the present work we report the use of polymersomes formed by amphiphilic block copolymers PMPC$_{25}$-PDPA$_{70}$ in PBS to encapsulate myoglobin under conditions close to those encountered within living cells. We show that confinement within polymersomes leads to a significant improvement in protein stability against thermal denaturation up to 95$^\circ$C at neutral pH. Circular dichroism, fluorescence and UV. VIS. were used to study the protein structure. The results showed little or no evidence of unfolding or reduced enzymatic activity. The latter parameter actually exhibits a two-fold increase after thermal cycling when the confined protein concentration is higher than 5% v/v. Our results suggest that nanoscopic confinement is a promising new route for the enhanced long-term storage of proteins. In conclusion, we provide strong evidence that protein thermodynamics within a nanoscopic aqueous environment are strongly affected by both concentration and confinement. More importantly, we demonstrate that proteins encapsulated within polymersomes can withstand large temperature gradients without compromising their structure (and hence their biochemical activity). This is very important in the context of polymersome-mediated delivery of proteins and/or the development of nano-reactors.

COLL 611

Self-cleaning, reusable templates for protein nanopatterning fabricated by interferometric lithography and nanoimprinting
The photocatalytic properties of titania are well-documented: absorption of UV photons causes oxidative degradation of organic molecules in close proximity to the oxide surface. Here we report the exploitation of this phenomenon for nanofabrication.

First, self-assembled monolayers (SAMs) of alkylphosphonates on the native oxide of a titanium film are used as a resist for exposure in a Lloyd's Mirror interferometer. Exposure to maxima in the interferogram causes selective photocatalytic degradation of the SAM and etching in piranha solution causes dissolution of the oxide and underlying metal in the exposed areas, yielding line widths as good as 22 nm with a variable but controllable period \( \lambda/2\sin\theta \). Interferometric lithography offers fast, simple, inexpensive routes to nanofabrication over macroscopic areas (cm²). Second, features imprinted in a spin-case film of titanium methacrylate monomer are cured then calcined to yield titanium nanostructures. For both methods, the native oxide at the surface of the Ti structures exhibits photocatalytic activity and is used to control protein adsorption.

Adsorption of an amine terminated alkyl phosphonate onto the titania nanostructures enables their functionalization with proteins, while adsorption of an oligo(ethylene glycol) terminated silane (OEG-silane) onto the substrate surface (silica) between the structures renders it protein-resistant. Alternatively, the entire sample is functionalized by adsorption of OEG-silane, and the titania regions rendered adhesive to proteins by irradiation by flooding the sample with near-UV light to cause photocatalytic removal of the OEG-silane from the Ti structures. In both cases, the proteins are completely removed by photocatalytic degradation via subsequent irradiation of the surface at 325 nm, while the OEG-silane adsorbed on silica remains intact. The titania regions may be functionalized using a different protein. The process may be repeated many times, offering a simple methodology for the presentation of nanostructured assemblies at surfaces over macroscopic areas.

COLL 612

Direct fabrication and characterization of Langmuir Blodgett films of reduced graphene oxides via pre-functionalization with thiols

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Fabrication of reduced graphene oxides (RGOs) thin films has been well documented with various methods via chemical or thermal reduction of graphene oxides (GOs) thin films. However, fabrication of RGOs or chemically functionalized RGOs thin films has been challenging by using RGOs or chemically functionalized RGOs because of bad dispersibility of RGOs or not developed suitable coating method. In this work, fabrication
and characterization of transparent conducting films have been demonstrated using thiol functionalized reduced graphene oxides, called “mercapto reduced graphene oxides (m-RGOs)”, in a facile and rapid process. The m-RGOs readily dispersed in various solvents including alcohols have allowed fabrication of m-RGOs thin films. Langmuir-Blodgett (LB) films of m-RGOs were obtained by transferring their Langmuir films, formed by simple drop casting of m-RGOs dispersion on water surface, onto various substrates including gold, glass and indium tin oxide. The m-RGO LB films showed low sheet resistances down to about 500 kΩ/sq at 92% optical transparency. The successful results make m-RGOs promising for applications in transparent conductive coatings, biosensing, etc.

COLL 613

Positive and negative nanolithography of graphite using DNA origami mask

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Graphene has many exceptional features recommending it for use in graphene-based bio-devices, such as the recently highlighted graphene nano-pores for DNA sequencing and a graphene–DNA biosensor. Nanoscale patterning of graphene will be necessary in order to fulfill its promise to integrate nano-electronic and optoelectronic devices into a wide variety of systems. Simultaneously. Several reports indicate that DNA Origami nanostructures, the form of scaffolded self-assembled DNA, which has recently evolved into a powerful tool to organize various molecules at the nanometer and even sub-nanometer scale, could be used as a masking material for nanolithography. In this report, for the first time, we shall demonstrate an outstanding and simple method to prepare negative or positive patterns on graphite using DNA nanostructure and controlled plasma pressure.
Fig. 1: a) Schematic illustration of plasma etching of HOPG using Cross-like DO (top right corner: cross-like DO with ssDNA anchor) as a mask. Low and high air pressure plasma respectively produces positive and negative patterns on HOPG; AFM topography images show DO patterning of HOPG with b) positive pattern and c) negative pattern created by specific pressure air plasmas; Insets: high resolution AFM images (right top corners) and line profiles.

To meet the challenge of binding origami masks rapidly on graphite, this paper will describe an approach in which the origami, rather than the graphene, is modified (illustrated in Fig. 1a top right corner). To meet the challenges of developing nanolithography, origami was used here as a lithography mask and no wet chemical processes were used for etching or to strip off the origami mask. To prepare positive or negative topography patterns of graphite/graphene different plasma pressures were used to switch the tone. Depending on the plasma pressure we demonstrate that origami can act as a mask to inhibit etching (Fig 1b) or as a catalyst to promote graphene/graphite etching (Fig. 1c), resulting in positive or negative patterns.

**COLL 614**

**Graphene-based fluorescent biosensors for heavy metal detection**

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This presentation demonstrates that graphene oxide can not only serve as a fluorophore but also serve as an energy acceptor in fluorescent biosensors. Graphene oxide is not vulnerable to photo-bleaching as compared to organic dyes; and it is environmentally benign and easy to be bio-conjugated as compared to quantum dots compared to inorganic semiconductor quantum dots. This presentation shows a graphene oxide-aptamer biosensor with graphene oxide as the fluorophore, which is built on the charge transfer principle. This biosensor shows a limit of detection as low as 0.92 nM for Hg(II). In addition, a CdSe/ZnS quantum dot-aptamer-graphene oxide composite biosensor has been developed based on the nano-metal surface energy transfer (NSET) process with graphene oxide as the energy acceptor. This biosensor has been used for detection of Pb(II) with a limit of detection of 90 pM.

**COLL 615**

**Novel biosensors for determination of phenolic compounds using catalyst-loaded reduced graphene oxide substrates**

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Sensors for the detection of hydrogen peroxide have come into the spotlight in recent decades due to the prevalent influence of the oxidative stress on numerous life processes including cell cycle, signaling pathways, defensive responses, unintended cell damage, etc. Non-invasive methods of H$_2$O$_2$ detection are important due to the implications of reactive oxygen species in the cell and DNA damage. The use of enzymatic biosensors has been the main way to detect hydrogen peroxide. However, the cost and difficulties in maintaining constant enzyme activity in enzyme-based sensory films has been a great disadvantage of these sensors. In this work, we have investigated novel sensors for hydrogen peroxide using catalyst-coated reduced-graphene oxide substrates. We have found that graphene oxide electrodes can be readily modified with Prussian Blue (PB) catalyst and reduced electrochemically to provide low ohmic-drop current-collection pathways. The presence of the reduced graphene oxide (rGO) has enabled achieving fast biosensor response to H$_2$O$_2$ ($t_{95\%} = 5$ s) and low limit of detection, LOD = 10$^{-8}$ M. We have also examined the means for reducing interference due to the ascorbic acid, a common antioxidant. We have developed a copolymer able to block the ascorbic acid waves while still maintaining a good response of the sensor to hydrogen peroxide. Furthermore, the immobilization of an enzyme (horseradish peroxidase or laccase) has enabled us to determine concentrations of phenolic species in various antioxidant media. The composite sensors designed are promising candidates for inexpensive and scalable sensors for hydrogen peroxide and testing of enzyme activity in synthetic and biological samples.

COLL 616

Graphene oxide-based FRET aptasensor on solid support

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Graphene oxide (GO) is attracting considerable interest in many basic and applied research fields including biosensing applications. By adsorbing dye-labeled aptamer on the GO surface, we can prepare the GO aptasensor. The fluorescence from the dye is not observed at the initial stage because of the fluorescence resonance energy transfer (FRET) process between the dye and GO, but it recovers when the aptamer forms complex with the target protein and the dye leaves from the GO surface.

As GO is readily dispersed in water, most GO aptasensors have been operated in an aqueous medium. By contrast, we have developed and studied a GO aptasensor fixed on a solid support. One advantage of our system is that we can directly observe phenomena occurring on the GO surface during protein recognition, using surface science analytical tools such as confocal laser scanning microscope (LSM) and atomic force microscope (AFM). To an identical single GO aptasensor fixed on SiO$_2$ surface, we observed the fluorescence recovery (by LSM) and the increase of the thickness (by AFM) after the recognition of the target protein. We also performed AFM observations in solution for observing protein recognition processes in situ.
Another advantage is that we can combine the sensor with microfluidics to realize an on-chip GO aptasensor. By fabricating the multichannel structure, we can examine several different samples at one time, which is useful for high-throughput analyses. The microfluidics technology is also used for fabricating GO aptasensor microarray, which integrates the different aptasensor probes in each channel. These developments are useful not only for the practical application of GO aptasensor, but also for the basic research such as a new probe design.

COLL 617

Graphene oxide-based amplified fluorescent biosensor for Hg$^{2+}$ detection through hybridization chain reactions

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We report a graphene oxide (GO)-based fluorescent sensor for Hg$^{2+}$ detection in aqueous solutions by using hybridization chain reactions (HCRs). GO is used as an adsorption material for capturing single-stranded DNA and an efficient fluorescence quencher for reducing the background signal. In the detection strategy, two hairpin probes and a helper DNA are employed. Without Hg$^{2+}$, they are adsorbed by the GO and the fluorescence of one of the hairpin probes is quenched. In the presence of Hg$^{2+}$, the HCRs between the two hairpin probes are initiated by Hg$^{2+}$ with the aid of the helper DNA through the T-Hg$^{2+}$-T coordination chemistry. The double-stranded DNA products of the HCRs are released by the GO and the fluorescence is recovered. The detection limit of the sensing method is 0.3 nM, which is sufficiently sensitive for practical applications. The sensing system also exhibits high selectivity against other divalent metal ions and the application of the sensor for drinking water shows that the proposed method works well for real samples.

COLL 618

Graphene oxide polymer hybrid and functionalized graphene for biological applications

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Graphene Oxide (GO) and its derivative have attracted great deal of attention to the biological community due to their low cytotoxicity. We have developed a facile route to covalently graft N-isopropylacrylamide (NIPAM) directly from the surface of exfoliated graphene oxide (GO) using free radical polymerization technique and different GO-PNIPAM (GPNM) hybrids by changing the weight ratio of the two are produced. The grafting of PNIPAM has been demonstrated by several techniques like NMR,
Raman, XPS, FTIR spectroscopy and TEM, AFM microscopy. The GO-g-PNIPAM hybrid shows ≈20 times increase of fluorescence property than GO in aqueous medium. The origin of FL property as well as gradual blue shift of emission peak in all the hybrids from that of GO, may be attributed due to the lowering of sp² cluster domain size, defect level transition and structural changes, since it is well documented that both the structure and defects influence the electronic structure of nanomaterials, subsequently changing their optical properties appreciably. We have studied the bio-compatibility evolution as well as cell viability using one of the GPNM hybrid solutions with different concentrations by conventional MTT assay. We have also loaded hydrophobic and hydrophilic drug using this bio-compatible and nontoxic GPNM hybrid, which has been demonstrated by UV-vis and fluorescence spectroscopic study. The loaded drug can also be released from the hybrid based on their affinity to biomolecules like DNA, RNA and the release of drug can easily be monitored by optical measurement like fluorescence property. Thus as synthesized material can be used as an important biological probe as drug carrier which will pave a new way to release the loaded drug.

**COLL 619**

**Enhanced kinetics of enzymatic nanosensors**

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Nanosensors employing quantum dots (QDs) and functional moieties such as enzymes offer tremendous promise for disease surveillance/diagnostics and chemical/biological threat activity as their small size permits cell penetration and their inherent photochemical properties (i.e., size tunable fluorescence, ease in attaching functional moieties, resistance to photobleaching, etc) are well-suited for rapid, optical measurement. The effectiveness of biorecognition agents (e.g., enzymes) immobilized on QDs are not completely understood, hindering development of in vitro, in vivo, or in situ chemical/biological sensors and remediation materials. We analyze enzyme effectiveness when attached to QDs using one model system and one illustrating an important biological threat application—the toxicity neutralization of paraoxon, a simulant nerve agent. Two sizes of QDs, 525 or 625 nm, were appended with DHLA ligands to improve aqueous stability and prevent aggregation. Rapid self-assembly of enzymes to the QD surface via spontaneous metal coordination of the oligohistidine tag onto the Zn²⁺-rich QD surface, required only the mixing of molar ratios of two reactants. We first use alkaline phosphatase, a hydrolase enzyme that converts 4-methylumbelliferyl phosphate to fluorescent methylumbelliferone, to illustrate improved enzyme kinetics on QDs (e.g., ≈20 to 30% increase in Vₘₐₓ). Next, we immobilize phosphotriesterase (PTE) onto distinctly sized QDs with various enzyme-to-QD ratios.
PTE catalyzes the detoxification of organophosphate pesticides (e.g., paraoxon, an analog of sarin) to \( p \)-nitrophenol. The optimal ratio of PTE to 525 nm and 625 nm QD’s was determined to be 6 and 8, respectively. At these ratios, we saw a \(~50 \text{ to } 60\%\) increase in \( V_{\text{max}} \) for PTE and other kinetic parameters. The enhanced enzyme performance in both cases is most likely due to increased enzyme-substrate interactions from enzyme orientation, enzyme density, and substrate diffusion on or near the QD. Development of these nansosensors as optical-based biosensors (e.g., within compact microfluidic devices) may greatly improve the sensitivity of conventional biological/chemical detection schemes.

**COLL 620**

**Multifunctional nanoplatforms for multidrug resistance pathogen detection and destruction from whole blood**

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Bloodstream infection with drug-resistant bacteria kill several million people every year. Here we will discuss our recent report on the development of multifunctional nanoplatforms for simultaneous targeted imaging and multimodal photodestruction of multi drug resistance bacteria in a whole-blood sample. Experimental data shows that it can be used for label-free detection and combined IR light driven therapy.

**COLL 621**

**SERS immunoassay based on analyte-mediated aggregation of gold nanoparticles**

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SERS based assays offer a number of potential advantages relative to conventional diagnostic platforms, including higher sensitivity and greater multiplexing capacity. Herein we describe our effort to develop a simple, rapid homogeneous SERS immunoassay based on analyte-mediated aggregation of gold nanoparticles. Gold nanoparticles are modified with a Raman reporter molecule and a molecular recognition element, e.g., antibody, to form an extrinsic Raman label (ERL). As well-dispersed particles, ERLs do not provide a hot spot and thus, do not produce a detectable SERS signal. In the presence of the antigen, the ERLs aggregate around the antigen thereby forming hot spots to facilitate SERS detection. Two model systems, influenza A virus and mouse IgG, are used to optimize reproducible formation of aggregates and establish proof-of-principle for the assay. Additionally, the size of the antibody used to modify the nanoparticles is implicated as the limiting factor in assay sensitivity.

**COLL 622**
Detection of rare pathogens at the single-cell level

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An agarose droplet microfluidic single-cell emulsion PCR (ePCR) method was developed for the analysis of rare pathogenic bacteria in the presence of large excess of normal bacteria. Genetic alternations can serve as highly specific biomarkers to distinguish fatal bacteria cells from their normal counterparts. However, these mutations normally exist in very rare amount in the presence of a large excess of non-mutated analogs, which posing significant difficulties for their detection. We have developed an agarose droplet-based microfluidic ePCR method for highly sensitive, specific and quantitative detection of rare pathogens in the high background of normal bacteria. Our method utilizes the capability of microfluidic chip to rapidly generate monodispersed droplets and the unique thermosensitive sol-gel switching property of agarose. A microfabricated agarose droplet generator that produces uniform picoliter agarose emulsion droplets for genomic analysis was developed and evaluated. PCR can be efficiently performed in agarose solution droplets, which are gelated to microbeads after PCR to capture amplicons and maintain the monoclonality of each droplet. Our results indicated single copy DNA can be efficiently amplified in agarose droplets and the resulting monoclonal beads can be easily manipulated for downstream analysis. Massively parallel singleplex and multiplex PCR at the single-cell level in agarose droplets was further successfully demonstrated. Moreover, we challenged the system with rare pathogen detection and realized the sensitive and quantitative analysis of single E. coli O157:H7 cell in the high background of 100 000 excess normal K12 cells. Such a multiplex single-cell agarose droplet amplification method enables ultra-high throughput and multi-parameter genetic analysis of large population of cells at the single-cell level to uncover the stochastic variations in biological systems. The capability of studying and enumerating low frequency pathogenic cells among large population of normal counterparts at the single-cell level will have great implication in fundamental research and clinical diagnostics.

COLL 623

Gold nanoparticles-based colorimetric logic gates for Pb^{2+} and Cr^{3+} detection

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Logic gate is the basic elements of calculation and logical operation in the computer science. In recent years, how to realize the logic systems between the functional molecules in the chemical and biological process is becoming a research hotspot through nanotechnology. In this study, gold nanoparticle is selected as the supporter of logic gates, instead of organic molecule, which avoids the complicated synthesis and improves the stability of logic gate. Considering the convenience of the logic systems, simply synthesis of gold nanoparticles and following surface functionalization are focused, and commercial (bio-) molecular are selected in this study. By building
concrete examples, urea was selected for the functionalization on the surface of gold nanoparticles based on its binding capability toward metal ions. Then the addition of either Pb$^{2+}$ or Cr$^{3+}$ could induce the aggregation of gold nanoparticles with obvious red-to-blue color changes. We define the blue and red color as output (1, 0), while the absence and presence of metal ions as inputs (0, 1). Then this colorimetric system shows an “And” logic behavior. The result can provide new strategies and theoretical basis for the exploitation of intelligent system, such as the molecular recognition, biological sensing, clinical diagnosis, and drug release and so on.

COLL 624

Functional DNA nanotechnology for selective detection of pathogens and biohazards

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Selective agents for pathogens and biohazards are very useful for applications such as environmental monitoring, food safety and medical diagnostics. However, designing selective agents based on a single class of molecules for a broad range of targets with high sensitivity and selectivity remains a significant challenge. Recent progress in nanoscale science and technology has resulted in a number of nanomaterials with interesting optical, electrical, magnetic properties that can be ideal choices for signal transductions for detection. However, most of these materials lack selectivity required for detection. Functional DNA, a new class of DNA with functions similar to either antibody (known as aptamers) or enzymes (called DNAzymes) can provide high selectivity for a wide range of pathogens and biohazards, including small molecular targets that antibodies do not bind with high selectivity. We have been able to use a combinatorial method called in vitro selection to obtain functional DNA that can bind targets of choice strongly and specifically, and used negative selection strategy to improve the selectivity. By labeling the resulting functional DNA with gold nanoparticles, quantum dots, and supermagnetic iron oxide nanoparticles, we have developed new classes of colorimetric and fluorescent sensors, and smart MRI contrast agents for pathogens and biohazards. A novel approach of using an inactive variant of functional DNA to tune the detection range of the sensors is also demonstrated. For even more straightforward field applications, these sensors have been converted into simple “dipstick” tests for qualitative detection. We have also applied the method to functionalize lanthanide-doped upconversion nanoparticles for sensing and imaging applications. These and other recent results will be presented.

COLL 625

Enzyme-based detection of infectious diseases in Point-of-Care settings
Infectious diseases, such as malaria, affect hundreds of millions of people primarily in the developing countries. Many of these regions lag the advanced laboratories and trained personal that are needed for fast and reliable diagnostics. As a consequence, patients are often insufficiently diagnosed, which then results in inadequate or overtreatment of the patients. These factors contribute to the increase in drug resistant parasite populations that have been experienced in recent years.

We are currently developing, sensitive and easy-to-use platforms for measuring patient infection levels of infectious diseases in the endemic countries. Recently, we published such a platform for measuring malaria infection levels in patients directly in a crude biological sample, \textit{i.e.} a drop of blood or saliva. This platform is based on the combination of droplet microfluidics and the specific detection of enzymatic reactions by the essential malaria enzyme \textit{Topoisomerase I} on a linear DNA substrate. Briefly, parasites, linear DNA substrate and lysis buffer are confined in picoliter droplets generated by the microfluidics chip. Topoisomerase I from the lysed parasites circularizes the DNA substrate. The droplets are then trapped in a droptrap devise, where they are evaporated and Rolling circle Enhanced Enzymatic Activity Detection (REEAD) is performed. In this way single enzymatic reaction events are visualized as fluorescent dots in a fluorescence microscope. Thus, the combination of droplet microfluidics and the REEAD technique makes detection of single reaction events possible with down to single parasite resolution. We are currently developing a readout method suitable for low-resource settings, so that the assay can be conducted in the field by non-expert users.

We expect that the presented platform, called REEAD-on-a-chip, may eventually contribute to point-of-care diagnostics, particularly in low-resource settings in developing countries.

\textbf{COLL 626}

\textbf{DNAzyme-coupled droplet microfluidics for detecting single bacteria in blood}

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Noscomial and community-acquired infection of deadly bloodborne pathogens is a major threat to public health. Moreover, emergence of multi-drug resistant pathogens is another immense challenge to maintain public health. Accurate detection of such pathogens at the early stage can help physicians to select proper antibiotics to save lives and lighten the economical burden to our society. However, unfortunately, blood culture method, the gold standard for the detection of bacteremia, takes several days to obtain results. Molecular diagnosis methods, such as polymerase chain reaction (PCR) and immunoassays are often not sensitive enough to detect bacteria that occur at low concentrations in blood (1-100 colony-forming unit (CFU)/mL). Moreover, all these techniques are sophisticated and expensive, and therefore not well-suited for routine testing. Therefore, simple methods are urgently needed for rapid and sensitive identification of bacteria in blood, which has the potential to significantly reduce the mortality rate and the cost of medical care associated with blood stream infections.

In this study, we have developed a droplet microfluidic system that integrates bacteria-specific DNAzyme sensors to detect bacteria in patient blood at single-cell sensitivity within a few hours. Our central hypothesis is that the confinement of bacteria in droplets significantly increases the concentration of released target molecules that can activate the DNAzyme sensors to produce detectable fluorescent signal in a rapid, real-time fashion. Specifically, infected patient blood is mixed with DNAzyme sensor solution including bacteria lysis buffer within the microfluidic channel which is encapsulated into millions of individual picoliter droplets. Because bacteria exist at low numbers in blood, we anticipate that each droplet contains one or no bacteria. DNAzyme sensors fluoresce instantaneously in the droplets that contain bacterium. The droplets are monitored by APD (avalanche photodiode) embedded confocal microscopy in a high throughput manner.

Our novel approach of integrating real-time DNAzyme sensors with droplet microfluidics bypasses many challenges faced by current techniques (e.g., blood culture) such as culture, isolation of genomic DNA which is required for PCR. This rapid detection and early intervention will therefore be significantly helpful of treating blood stream infections and reduce mortality.

**COLL 627**

**Point-of-care magnetic platforms for molecular analyses of pathogens**
Magnetic biosensors, based on nanomaterials and miniature electronics, have emerged as a powerful platform for molecular analyses of pathogens in biological samples. Magnetic sensing allows for rapid and highly selective detection, as it is free from interference from biological background. This talk will present a review on this technology with topics including magnetic nanomaterials, labeling strategies, and novel magnetic devices specifically developed for biological/clinical applications. These methods are combined into point-of-care diagnostic platforms that are capable of rapid and specific profiling of pathogens directly in clinical samples. We utilized this platform to detect various clinically relevant bacterial strains including *M. tuberculosis*, *S. aureus*, *S. pneumoniae* in whole blood and sputum, with sensitivity down to single bacterium within 2.5 hours.

**COLL 628**

SERS-based competitive immunoassay of dual cardiac markers for early diagnosis of acute myocardial infarction nanosensor

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There have been compelling evidences that the early diagnosis of acute myocardial infarction (AMI) involves the determination of the serum levels of a group of cardiac biomarkers. Among the most frequently used biomarkers, the simultaneous estimation of CK-MB and cTnI marker levels in blood, shortly after the AMI incidence, greatly contributes to the clinical applicability for the early diagnosis of AMI. Recently, the surface-enhanced Raman scattering (SERS)-based immunoassay technique using functional nanoparticles has attracted significant attention due to its multiplexing potential and fast detection capability. Because Raman bands are 10-100 times narrower than fluorescence bands, the SERS technique has been acknowledged as a potential candidate for multiplex detection. Moreover, only a few seconds are needed for the simultaneous detection of multiple biomarkers. Here, we demonstrate a SERS-based competitive immunoassay for simultaneous determination of CK-MB and cTnI. The competitive assay requires no sample processing, beyond centrifugation or filtration to remove particulates, and is significantly less sensitive to sample dilution and sample matrix effects than the sandwich immunoassay format. Therefore, it provides much tighter data with lower variability between duplicate samples and lower variability between assays. Furthermore, the competitive assay requires a shorter detection time than the sandwich immunoassay because only one binding process between antigen and antibody is needed. In the present study, the simultaneous SERS detection of CK-MB and cTnI cardiac markers in blood serum was achieved under a single excitation
wavelength. This novel immunoassay has multiple advantages including a quick assay time (less than 15 min), a non-washing step (just magnetic beads separation), and simultaneous multiple marker detection using reliable, sharp, and easily distinguishable SERS peaks.

Workflow of suspension competitive immunoassay for the detection of two cardiac markers includes a) preparation of probes.

COLL 629

Rapid cell-free nucleic acid detection using micro-encapsulation system

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DNA, mRNA and microRNA are released and circulate in blood. Recent clinical studies have revealed the presence and extent of cell-free nucleic acid (cfNAs) in peripheral blood correlates with tumor aggressiveness and clinical outcome. Comparing with cancer protein blood biomarkers, cfNAs can be more informative, specific and accurate. Therefore, detection of cell-free nucleic acid is becoming a powerful tool for cancer diagnosis and prognosis, managing during therapy, and for personalized medicine.

Traditional methods for cfNAs analysis including qPCR, gene array and sequencing for gene mutations, methylation, DNA integrity, microsatellite alterations, and viral DNA
detection in blood. However, these methods are complex, expensive and time consuming. In particular, a crucial factor in cfNAs detection is cfNAs extraction which results in major batch-to-batch variations.

Here, we describe a procedure allowing highly sensitive detection of cfNAs in a quantitative manner directly from serum with minimal sample preparation and pretreatment. The method is based on using a droplets-based microfluidic system for compartmentalization of sample and droplet digital nucleic acid amplification (DDNAA) to detect cfNAs in serum. Our central hypothesis is that the confinement of cfNAs in pico-litter droplets significantly increases sensitivity and selectivity for cfNAs detection in a rapid fashion. Since compartmentalization of blood within picoliter droplets, minimal blood components can be encapsulated in droplets with single cfNAs and this can minimize the interference effects from blood components such as protein, and other NAs.

We demonstrate the accurate and sensitive quantification platform technology for cfNAs detection in serum without cfNAs extraction, which solves one of the biggest issue in cfNAs analysis field. Furthermore, our rapid cell free nucleic acid detection system can be applied to monitor various targets such as circulating tumor cells, bacteria, virus and fungus.

**COLL 630**

**Cancer biomarker detection in urine with nanometer-scale virus-plastic electrodes**

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Interrogating patient samples for disease diagnosis could be more rapid, less expensive and more routine, if the molecular recognition necessary for disease marker identification could be coupled directly to an electronic signal. Towards this goal, the Weiss laboratory collaborates with electrochemist Prof. Reg Penner to directly wire viruses into electronic circuits. Using phage display and synthetic chemistry to engineer the viral surfaces provides an inexpensive and very effective platform for biomarker recognition. A composite surface of engineered viruses and the conducting polymer, PEDOT, could be electrodeposited onto electrodes for fabrication of sensitive area detectors for direct, cancer biomarker readout in synthetic urine.

**COLL 631**

**Sunlight-driven hydrogen formation by membrane-supported photoelectrochemical water splitting**
We are developing an artificial photosynthetic system that will utilize sunlight and water as the inputs and produce hydrogen and oxygen as the outputs. We are taking a modular, parallel development approach in which three distinct primary components—the photoanode, the photocathode, and the product-separating but ion-conducting membrane—are fabricated and optimized separately before assembly into a complete water-splitting system. The design principles incorporate two separate, photosensitive semiconductor/liquid junctions that will collectively generate the 1.7-1.9 V at open circuit necessary to support both the oxidation of H₂O (or OH⁻) and the reduction of H⁺ (or H₂O). The photoanode and photocathode will consist of rod-like semiconductor components, with attached heterogeneous multi-electron transfer catalysts, which are needed to drive the oxidation or reduction reactions at low overpotentials. The high aspect-ratio semiconductor rod electrode architecture allows for the use of low cost, earth abundant materials without sacrificing energy conversion efficiency due to the orthogonalization of light absorption and charge-carrier collection. Additionally, the high surface-area design of the rod-based semiconductor array electrode inherently lowers the flux of charge carriers over the rod array surface relative to the projected geometric surface of the photoelectrode, thus lowering the photocurrent density at the solid/liquid junction and thereby relaxing the demands on the activity (and cost) of any electrocatalysts. A flexible composite polymer film will allow for electron and ion conduction between the photoanode and photocathode while simultaneously preventing mixing of the gaseous products. Separate polymeric materials will be used to make electrical contact between the anode and cathode, and also to provide structural support. Interspersed patches of an ion conducting polymer will maintain charge balance between the two half-cells.

Investigation of the impact of LiCoO₂ nanoparticles on model organisms Shewanella oneidensis and Daphnia magna

While many previous studies have investigated the behavior of simple metal oxides, emerging technologies such as energy storage are utilizing more complex and multi-component metal oxides consisting of layered structures and redox-active metals. The widespread use of such materials increases the potential for unintentional release and therefore, analyzing their interaction with biological systems is of the utmost importance. We are using LiCoO₂ as a model system for assessing the potential environmental...
impact of technologically relevant nanomaterials for energy storage. LiCoO₂ is a redox-active material that is being utilized in cathodes of Li-ion batteries. We have synthesized LiCoO₂ nanoparticles via a flux-based method to yield plate-like structures under 50 nm in diameter and several atomic layers in width. The impact of these particles on model organisms was investigated. Specifically, respirometry was used to investigate bacterial growth rates for *Shewanella oneidensis*, a single cell model system. These studies reveal dose-dependent inhibition of bacterial growth and recovery from initial inhibitory effects of LiCoO₂ nanoparticles based on the degree of particle aggregation. Additionally, acute response experiments to LiCoO₂ nanoparticles were also completed with *Daphnia magna* as a multicellular organism model for comparison.

COLL 633

Effects of anodic potential and chloride ion on overall reactivity in semiconductor electrochemical reactors

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We have investigated electrochemical treatment of real domestic wastewater coupled with simultaneous production of molecular H₂ as useful by-product. The electrolysis cells employ multi-layer semiconductor anodes with electro-active bismuth-doped TiO₂ functionalities and stainless steel cathodes. DC-powered Laboratory-scale electrolysis experiments were performed under static anodic potentials (+2.2 or +3.0 V NHE) using domestic wastewater samples, with added chloride ion in variable concentrations. Greater than 95% reductions in chemical oxygen demand (COD) and ammonium ion were achieved within 6 hours. In addition, we experimentally determined a decreasing overall reactivity of reactive chlorine species towards COD with an increasing chloride ion concentration under chlorine radicals (Cl⁻, Cl₂−∙) generation at +3.0 V NHE. The current efficiency for COD removal was 12% with the lowest specific energy consumption of 96 kWh kg/COD at the cell voltage of near 4 V in 50 mM chloride. The current efficiency and energy efficiency for H₂ generation were calculated to range from 34 to 84% and 14 to 26%, respectively. The hydrogen comprised 35 to 60% by volume of evolved gases. The efficacy of our electrolysis cell was further demonstrated by a 20 L prototype reactor totally powered by a photovoltaic (PV) panel, which was shown to eliminate COD and total coliform bacteria in less than 4 hours of treatment.

COLL 634

Transformation of redox active iron and cerium oxide nanoparticles at environmental interfaces

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Nanoparticles released into the environment could act as heterogeneous nucleation sites to incorporate toxic elements and molecules into a “hybrid” engineered/natural nanoparticle composite. To achieve a better understanding of the fate and transport of iron and cerium oxide nanoparticles, we studied two important cases: *in situ* nucleation and growth of iron oxide nanoparticles in the presence of arsenic, and the stability changes of engineered cerium oxide nanoparticles in the presence of ferrous ions. We utilized a simultaneous small angle X-ray scattering (SAXS)/grazing incidence SAXS setup to monitor *in situ* nucleation and growth of iron oxides on quartz. To characterize changes in metal oxide nanoparticle phases, we used atomic force microscopy, electron microscopy, Raman spectroscopy, and X-ray absorption spectroscopy. This study provides a quantitative and qualitative depiction of the evolution of important redox reactive metal oxide nanoparticles at dynamic environmental interfaces.

**COLL 635**

**Characterizing ion adsorption on the surface of synthesized nanoparticles: A combined theoretical and experimental approach**

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Poorly crystalline iron and aluminum oxyhydroxide nanoparticles with Keggin-type structural features are considered some of the most effective materials for adsorption of toxic heavy metals, radionuclides, and oxyanions. While the adsorptive capabilities of these particles have been established, identification of the specific reactivity factors and a mechanistic understanding of the adsorption process is lacking. To gain insights into these processes, polyaluminum Keggin-type species with diameters between 1-2 nm are probed using both experimental and theoretical methods. In the current study, the well known Al$_{30}$ molecule has been chosen as a model compound to investigate the adsorption of heavy metal (Cu$^{2+}$, Pb$^{2+}$, Zn$^{2+}$) cations and phosphate, arsenate, sulfate, and chloride anions. Al$_{30}$ nanoparticles with adsorbed contaminants were crystallized and their structural characteristics were determined using single crystal X-ray diffraction. Density Functional Theory (DFT) was utilized to determine the relative stability of the experimentally determined molecules and provide a more detailed understanding of the reaction mechanism. For the heavy metal cations, the DFT energetics associated with the step-wise reaction schemes indicated that the counter-ion present in solution plays an important role in the adsorption process.

**COLL 636**

**Time dependent transformations of ceria and silver nanoparticles during synthesis, storage, and in biological media**

Silver and ceria nanoparticles are in wide use in a variety of industrial, medical and consumer applications. Both beneficial and undesirable effects of these nanoparticles depend upon several factors including particle size, structure, and surface chemistry. In several circumstances these defining characteristics of nanoparticles will change as particles are processed, stored or dispersed in the environments of interest. As part of studies related to the understanding the impacts of ceria and silver particles on biological systems we have examined the influence of solution environments on the agglomerate size, chemical state and structure of ceria nanoparticles and the influence of these environments as well as particle structure and solution loading on the dissolution of silver particles in biologically relevant environments. The studies have involved the use of DLS measurements of particle size, analytical TEM examination of particle size, morphology and chemistry, XPS measurements of surface composition and chemical state, optical measurements to determine chemical state and solution concentration, and ICP-MS to understand dissolution. Changes in the oxidation state of Ce are particularly important for therapeutic applications of ceria. Using laser Raman and microXRD, we have found that ceria particles smaller than 8 nm have a dramatic change in physical structure as the oxidation state switches between +3 and +4. These changes in structure do not occur for particles larger than 20 nm. Understanding the biological impacts of silver particles requires knowledge of both the nature of silver particles in solution and the concentration of silver dissolved in the media. We have found that the solubility of silver nanoparticles depends upon the synthesis method and particle structure. For both silver and ceria particles the addition of fetal bovine serum proteins stabilizes particle size and solution suspension. However these proteins play a significant role in increasing the dissolution of silver.

COLL 637

Changes in nanoparticle properties detected inside organelles using high resolution fluorescence and X-ray microscopy in intact hydrated cells

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The growing use of engineered nanoparticles (NPs) in industrial and medical applications is expected to increase unintended environmental or occupational exposures and intended medical or direct consumer exposures. The physical and chemical properties of the NPs engage and activate distinct proteins and cellular pathways that, in turn, govern the impact of the NPs on the cell and ultimately on human health. The relationship between particle properties and these complex cellular processes and responses are still unclear. The difficulty in identifying these relationships is partially due to the strong tendency of NPs to acquire different properties in different environments. To better understand these relationships in the intracellular environment, we employ approaches that allow us to determine physical and chemical properties of the NPs inside intact cells and organelles. Here we describe changes in properties of zinc oxide NPs (ZNPs) and ceria NPs (CNPs) inside the cytoplasm and organelles of intact alveolar epithelial cells, which present a vulnerable target for airborne inhaled NPs. Using a highly sensitive fluorescent indicator for zinc ions, we quantified the dissolution dynamics that airborne ZNPs, deposited intact at the cell surface-air interface, undergo inside distinct organelles. We show that the impact on the cell is highly dependent on the type of organelles in which the dissolution occurs. We also describe the development of a correlated x-ray (STXM) and super resolution fluorescence (SIM) microscopy to study the changes in the oxidation state of CNPs inside organelles in intact cells. We show a clear shift to a higher Ce$^{3+}$ content in NPs that enter the cellular environment and point to possible interactions that might underlie the cellular response.

**COLL 638**

**Tuning the frictional properties of surfaces with nanoscale roughness using SAMs and graphene-SAM composites**

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Control of friction is a widely recognized problem that covers a broad range of materials from medical implants, to engines, to micro- and nano-scaled machine technologies. A ubiquitous challenge in many of these applications is how to control the wear that occurs in sliding contacts, which are dominated by the interactions between nanoscaled surface asperities, where the high pressures and shear forces that are experienced can result in increased friction and ultimately lead to device failure. Obtaining an atomic/molecular scale understanding of the interactions and energy dissipation mechanisms in asperity-asperity contacts at such interfaces is paramount for the rational design of new materials or lubrication schemes. We have developed a model platform to investigate true nanoscaled asperity-asperity contacts using silica nanoparticles deposited on a Si support to form surfaces with asperities of controlled radius of curvature (ca. 5 – 20 nm), matching those found in most machined interfaces. Friction, adhesion and wear at these surfaces are then explored using AFM where the AFM tip, acting as a single mobile asperity, allows us to probe asperity-asperity contacts. Molecular adlayers on silica, such as self-assembled monolayers (SAMs) can
dramatically reduce friction in such interfaces, however they can be easily damaged during impact and shear. A challenge with these molecular adlayers is that nanoscale surface roughness impacts both the formation and quality of the SAMs, as compared to those formed on atomically smooth surfaces, decreasing film stability. Using AFM, IR spectroscopy and MD simulations, we have explored how the interplay of high pressure, surface curvature and molecular forces come together to control friction at the atomic/molecular level in asperity-asperity silica contacts. New approaches for friction modification of interfaces, including the deposition of single and few-layer graphene and graphene-SAM composites have also been examined and will be described.

COLL 639

Frictional properties of graphene on hydrophilic and hydrophobic silica surfaces with nanoscale roughness

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Microelectromechanical system devices (MEMS) suffer from severe wear and short lifetimes from high pressure asperity-asperity contacts due to the nature of their rough surfaces. Recently nanoscale carbon lubricants, such as graphene, are of interest as protective surface coatings for MEMS. Here, Atomic Force Microscopy (AFM) has been used to investigate the frictional properties of graphene on hydrophilic and hydrophobic nanoparticle films, which model the nanoscaled asperities found on realistic surfaces. These AFM studies revealed that graphene partially conforms to the rough surfaces and as the number of layers increase, conformity decreases due to stiffening of the thicker layers, but increases under mechanical loading. Friction nominally decreases as a function of layer thickness, but was also found to depend on contact area of the tip and interfacial shear strain of the graphene associated with its adhesion to the substrate.

COLL 640

Elucidating atomic-scale wear processes in hydrocarbon-based materials via molecular dynamics and AFM

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Molecular dynamics (MD) simulations are unique in their ability to elucidate atomic-scale phenomena because the positions, velocities, and forces of all atoms in the system are known as a function of time. Atomic-scale wear in nanoscale contacts is of particular importance for tip-based nanomanufacturing applications. As a result, wear resistant materials, such as diamond-like carbon (DLC), have been used to coat AFM tips to improve the lifespan and reliability of AFM probes. We have performed atomic force microscope (AFM) experiments and MD simulations aimed at examining adhesion
and wear in diamond, ultrananocrystalline diamond (UNCD), and amorphous carbon (a-C:H) materials. We examine the normal and sliding contact of different shaped axisymmetric tips, composed of a-C-H and UNCD, with hydrocarbon-based substrates. The effects of tip shape, material, surface termination, impact point, and roughness on adhesion and wear were examined. Results from the MD simulations were compared, and lend insight into, adhesion data obtained in AFM experiments. The application of continuum mechanics models to data obtained using the AFM to extract work of adhesion values will also be discussed. Finally, we will describe the use of finite element analysis to create a unique tip geometry for MD simulations that maximizes contact area so that it approximately equals the contact size in complementary AFM tapping-mode experiments. The wear behavior of AFM tips coated with a common type of DLC, amorphous hydrogenated carbon (a-C:H), when it is scanned against an ultrananocrystalline diamond (UNCD) sample using amplitude modulation (AM) AFM and molecular dynamics (MD) simulations was compared. Both the AM-AFM and the MD results reveal gradual wear of a-C:H with no sign of fracture or plastic deformation. The atomistic wear events observed in the simulations are correlated with under-coordinated atomic species at the surface. For example, in the figure below the red carbon atom from the DLC tip (upper surface) began the simulation with a coordination number of 2, and the green carbon atom began the contact simulation with a coordination number of 1 on the UNCD (lower) surface. Other carbon atoms are represented as gray or blue spheres and hydrogen atoms on the DLC are represented as small white spheres.
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Recent atomic force microscopy studies of nanoscale single asperity contacts reveal surprising behavior related to chemical influences. First, for atomic-scale stick-slip friction for 2-dimensional materials including graphene, friction depends strongly on the number of 2-D layers\(^1\). This arises from the combined effects of high flexibility and variable substrate interactions that occur for atomically-thin sheets. An even stronger effect occurs when graphene is fluorinated. This is attributed to a different effect: the enhanced corrugation of the interfacial potential due to the highly localized charge at fluorinated sites, consistent with the Prandtl-Tomlinson (PT) model.

Second, we have demonstrated the ability to characterize single-asperity wear at high resolution by performing in-situ wear tests inside of a transmission electron microscope (figure below). For silicon tips slid against diamond, the shape evolution and volume loss due to wear are well described by chemical kinetics model based on stress-assisted bond formation and breaking mechanisms\(^2\). This allows new insights to be gained about the kinetics of atomic-scale wear\(^3\).

Polymer substrates with a built-in capability for alignment of nanometer-sized objects are of interest for the development, performance, and large-scale production of robust, flexible devices. We have used atomic force microscopy (AFM) in friction mode to investigate the effects of uniaxial stretching on the nanoscale adhesion and friction of glassy polymer substrates. Examples will be shown of the different friction responses of semi-crystalline and amorphous polymers along and across the stretching direction, and how this friction response is altered as the strength of adhesion between the polymer and the AFM tip is deliberately changed.

Surface chemistry of colloidal nanocrystals – from semiconductors to metal oxides

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About 50% of the atoms in crystals a few nanometer in diameter are surface atoms, a number highlighting the importance of surfaces in nanocrystal science. In the case of colloidal nanocrystals, attempts to elucidate their surface chemistry quickly followed the development of synthesis procedures. A general picture that applies to a wide range of II-VI and III-V semiconductors was however only established in the last 5 years, where it was found that the ligand coordination is close linked to the nanocrystal stoichiometry.¹ Ligands classified as X-type, such as carboxylates, phosphonates or thioliates proved to bind tightly to cation-rich nanocrystals, with an overall ligand:excess cation stoichiometry that makes for charge-neutral nanocrystals.² Ligands classified as L-type, such as amines or phosphines were typically weakly binding to stoichiometric
nanocrystals. In this contribution, we extend this prevailing picture by analyzing binding of amines to CuInS$_2$ and of carboxylates to HfO$_2$ and ZrO$_2$ nanocrystals.

We use solution $^1$H NMR in combination with elemental analysis to investigate the surface chemistry of CuInS$_2$ nanocrystals synthesized in the presence of amines. Opposite from known results on various nanocrystals (CdSe, CdTe, PbS, ZnO), we find that as-synthesized nanocrystals are capped by tightly bound amine ligands that show no indication of self-exchange at room temperature. Nevertheless, using in-situ heating experiments in a solution NMR spectrometer, we demonstrate the amine are involved in an adsorption/desorption equilibrium, opposite from typical X-type systems such as CdSe/carboxylate. We thus conclude that amines bind to the CuInS$_2$ nanocrystals as L-type ligands, a result in line with the stoichiometric Cu:In:S ratios in these nanocrystals. These findings are used to rationalize the outcome of different ligand exchange reactions, where we found that amines could be replaced by thiols but not by carboxylic acids.

We synthesized HfO$_2$ nanocrystals from HfCl$_4$ using a surfactant-free solvothermal process in benzylalcohol and found that the resulting nanocrystals could be transferred to apolar media using a mixture of carboxylic acids and amines. Using solution $^1$H NMR and elemental analysis, we studied the details of the transfer reaction and the surface chemistry of the resulting sterically stabilized nanocrystals. As synthesized nanocrystals are charge-stabilized by protons, with chloride acting as the counterion. Treatment with only carboxylic acids does not lead to any binding of ligands to the HfO$_2$ surface. On the other hand, we find that the addition of amines provides the basic environment in which carboxylic acid can dissociate and replace chloride. This results in stable apolar dispersions of HfO$_2$ nanocrystals, sterically stabilized by carboxylate ligands. However, titrations with deuterated carboxylic acid show that the charge on the carboxylate ligands is balanced by co-adsorbed protons. Hence, opposite from the X-type/non-stoichiometric nanocrystals picture prevailing in literature, one should look at HfO$_2$/carboxylate nanocrystals as systems where carboxylic acids are dissociatively adsorbed to bind to the nanocrystals. Since similar results were obtained with ZrO$_2$ NCs, this could be a general picture for the surface chemistry of metal oxide nanocrystals with important consequences on the chemistry of ligand exchange reactions.


Ligand exchange and the stoichiometry of metal chalcogenide nanocrystals

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I will describe the binding and displacement reactivity of excess metal cations on metal chalcogenide nanocrystal surfaces in the presence of Lewis basic ligands. We show this reaction is rapid and reversible leading to nanocrystal stoichiometries that depend sensitively on the solution concentration. The importance of this behavior to luminescence quantum yields and nanocrystal purification will be discussed.

In situ analysis of the formation of cationic naked nanocrystals generated under equilibrium control

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Colloidal nanocrystals exhibit a number of exciting properties that make them useful for energy storage and conversion, electrochromics, and other applications. In these devices, it is desirable to control their spatial arrangement in active layers, often with periodic meso- to macroscale architectures. Such control can be realized through block copolymer-directed assembly of ligand-stripped, or naked nanocrystals. Here, we will present recent progress understanding and controlling the chemical processes that ultimately yield stable dispersions of cationic naked nanocrystals. In particular, we will discuss the importance of reversible Lewis acid-Lewis base adducts formed during key steps in the reaction mechanism, which has allowed us to produce the first known stable dispersions of cationic naked lead selenide nanocrystals. The approach outlined
here is general for controlling the surface chemistry of a wide variety of metallic, metal oxide, and semiconductor nanocrystals.

COLL 646

Probing ligands on quantum dots by vibrational sum frequency generation spectroscopy

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We report measurements of the intra- and intermolecular ordering of tight-binding octylphosphonate ligands on the surface of colloidal CdSe quantum dots (QDs) within solid state films, and the dependence of this order on the size of the QDs. The order of the organic ligands, as probed by vibrational sum frequency generation (SFG) spectroscopy, decreases as the radius of the QDs decreases; this decrease is correlated with a decrease in the order of underlying Cd2+, as detected by X-ray photoelectron spectroscopy (XPS) line width measurements, for radii of the QDs, \( R > 2.4 \) nm, and is independent of the disorder of the Cd2+ for \( R < 2.4 \) nm. We believe that, for \( R < 2.4 \), the decreasing order of the ligands with decreasing size is due to an increase in the curvature of the QD surfaces. Disorder in the Cd2+ results from the presence of a shell of Cd2+-surfactant complexes that form during synthesis, so this work demonstrates the possibility for chemical control over molecular order within films of colloidal QDs by changing the surfactant mixture.

COLL 647

Probing surface of colloidal nanocrystals with potentiometry

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Development of colloidal nanomaterials has impacted many areas of materials design. There are extensive R&D efforts toward using nanocrystal-based materials in light-emitting devices, electronic circuits, solar cells and other electronic and optoelectronic devices. However, we have very little understanding of dynamic processes that occur at the nanocrystal surface during synthesis and post-synthetic modifications. The field also lacks techniques for in situ monitoring of surface chemistry. We show how electrochemistry can be used to study the surface of colloidal nanocrystals under realistic reaction conditions. We have performed potentiometric titrations of CdSe quantum dots and nanoplatelets at different temperatures in polar and non-polar media, quantified the affinity of ligands to the nanocrystal surface, and studied reaction kinetics at nanocrystal surface. This study showed that potentiometry is a powerful technique to measure the active surface area of nanocrystals of different size and shape in solution, to probe the reaction dynamics, and to determine the affinity of the ligands to the
Moreover, potentiometry can provide real time feedback during SILAR synthesis of core-shell nanostructures.

**COLL 648**

**Adsorption of halides and oxygen on the PbSe quantum dots: DFT calculations**

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Using density functional theory (DFT) and time dependent DDFT (TDDFT), we simulate the oxidation process on the surface of Pb_{16}Se_{16} and Pb_{68}Se_{68} QDs and its effect on their electronic and optical properties. When oxygen is substituted for Se ions, the electronic properties of the QD are insignificantly perturbed. In contrast, if oxygen is adsorbed on the QD surface and coordinated with two Pb ions, it introduces additional unoccupied states inside the QD’s band gap, so called mid-gap states. Such states are hybridized between the oxygen and the QD’s surface atoms and contribute to the lowest-energy optically dark or semi-dark transitions likely resulting in quenching of the QD luminescence. In contrast, if the oxygen is coordinated with Se and Pb ions on the surface, the mid-gap states are not present and the optical transitions are similar to those of the non-oxidized QDs. Similar behavior was also found for halide radicals. However, the trap states are eliminated for halides in their ionic form or in a form of lead salts (PbCl_{2} or PbI_{2}). The presence of other surface ligands such as primary amines insignificantly affects the electronic structure of QDs, but increases the binding energy of neighboring halide ions, favoring their attachment to the (111) and (110) surfaces of the PbSe QDs.

**COLL 649**

**Quantum dot solids with well-controlled electronic properties via halide passivation**

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The term quantum dot (QD) solid is used to describe arrays composed of colloidal nanocrystals which embody unique and tunable quantum confinement-induced benefits yet possess long-range electronic transport necessary for device applications. Attention in the past has been focused on removal of native ligands during QD solid formation to enable electronic wavefunctions to overlap between neighboring QDs with use of strongly bound thiols. Recent results show that additional halide ions can enable much greater control over electronic properties of the solid, and thus enable insight into constructing films with desired characteristics. Application of the halides can occur during synthesis, during QD solid formation, or during post processing. Resulting
properties of QD solids for high performance optoelectronic device applications will be discussed.

**COLL 650**

One pot high yielding approach to a covalent "Ensamble" of polyhydrosiloxane, carbon nanotubes, and Pt-nanoparticles

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Attachment of metal nanoparticles onto the surface of carbon nanotubes is a very interesting approach to produce metal nanoparticle-nanotube composites for their utility in various applications such as catalysis and molecular sensing. In recent years, elegant strategies to produce such composites have been devised, which reliably provide functionalized materials in good yields. But due to the limited availability of such materials their applications has been quite limited in scope.

In this presentation, we will disclose a new and high yielding route which we have devised to fabricate carbon nanotube-Pt nanoparticle composites in one pot. This strategy is based on our previous work where well defined poly(methylhydro)siloxanes are covalently attached to carbon nanotubes via alcoholsysis reaction of hydroxyl carbon nanotubes. In the same pot, Pt precursors were added, which produced Pt-nanoparticles attached to nanotubes via polysiloxanes. The resulting composites were analyzed by various techniques and their property profiling was carried out using NMR, IR, TEM, and SEM techniques. We also have carried out mechanistic studies of the production and attachment of Pt-nanoparticles onto the carbon nanotube surface. In addition we will also present the catalytic activities of Pt-functionalized carbon nanotubes.

**COLL 651**

SiC-Co hybrid nanowires: Fabrication, electronic structure, and absorption on electromagnetic waves

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Serious electromagnetic interference pollution, the fourth and growing source of pollution, is omnipresent and presents extensive threats to biological systems by promoting cancer, inducing breakdown of DNA strands and weakening immune system. It is highly demanded to develop high-performance microwave absorbers to address this issue. By using layer-by-layer assembly, we have synthesized dielectric-magnetic SiC-Co hybrid nanowires in which the inner is SiC nanowire and the outside is covered
with uniform Co nanoparticles. The decoration of Co on SiC nanowires could be easily tuned by controlling the reaction time. The electronic structures were studied by analyzing their Si K-edge, Si L-edge, O K-edge and Co L-edge X-ray absorption near-edge structures. It is found that charges are redistributed in the hybrids through Si-O-Co bondings, which lead to the complementarity between the dielectric loss and magnetic loss. Under an altering electromagnetic field, the synergetic interaction between magnetic and dielectric components extensively attenuate microwaves. The excellent microwave absorption ability endows them with great potential as materials for microwave absorption applications.

**COLL 652**

**Functionalized graphene oxide as a potential carrier for drug and gene delivery**

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**INTRODUCTION**

Graphene has shown promising applications in many fields including gene and drug delivery owing to its ability to traverse the plasma membrane and, hence, promote cellular uptake of small molecules [1] and macromolecules [2]. Graphene and its derivatives have been investigated for biological applications because of their biocompatibility, unique conjugated structure, relatively low cost and availability on both sides of a single sheet for drug binding [3]. Graphene oxide (GO), prepared by the chemical oxidation of graphite has the advantage of being well-dispersed in water and physiological environments. Owing to its small size, intrinsic optical properties, large specific surface area, low cost and useful covalent/non-covalent interactions, GO has proved itself to be a promising new material for biological and medical applications [4,5]. In the present work, GO was covalently functionalized with polyvinyl alcohol, Pluronic F127, Tween 80 and maltodextrin in order to enhance its solubility and biocompatibility. Poorly water soluble anticancer drugs, camptothecin and ellagic acid, were loaded onto functionalized GO as carrier and the drug loading and cytotoxic activity of drug loaded onto functionalized GO were evaluated. GO was also functionalized with poly(ethylene glycol) bis(amine), polyethylenimine, polyarginine and poly-L-lysine to aid in loading RNA for RNA delivery.

**EXPERIMENTAL METHODS**

GO was functionalized via the EDC and NHS reaction leading to the formation of ester/amide linkage. For loading the drug, solution of anticancer drugs in DMSO was added to the functionalized GO dispersed in water. Excess drug, not loaded, was removed by centrifugation and dialysis. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), particle size and zeta potential analyzer, and UV-vis spectra were used to characterize the samples. Next we investigated the in-vitro cytotoxic activity of functionalized GO with and without drug using cancer cell lines.
RESULTS AND DISCUSSION
The ester/amide bond formation between the carboxyl groups on GO and hydroxyl/amine groups on polymers was confirmed by the FTIR spectra. TGA analysis was used to calculate the amount of polymer covalently attached to GO. It was found that drugs could be complexed with GO by directly mixing drug solution with functionalized GO aqueous solution. The binding of drug to the functionalized GO could be attributed to the π-π stacking and hydrophobic interactions between drug and aromatic regions of the graphene sheets. The UV-vis spectra was used to indicating the successful loading of drug onto GO. The experiments to load RNA onto functionalized GO are currently ongoing and results will be reported later. GO functionalized with poly(ethylene glycol) bis(amine), polyethylenimine, polyarginine and poly-L-lysine is being used for RNA loading.

Cell toxicity tests for the functionalized GO were carried out using MCF7 human breast cancer cells. No significant toxicity was found even at higher concentrations (400 μl/ml) when the MCF7 cells were incubated with functionalized GO. Therefore, functionalized GO is not cytotoxic and can be used for the drug and gene delivery. In MCF7 cells, the cytotoxic activities of the functionalized GO loaded with anticancer drug was higher than the drug alone. These results suggested that the functionalized GO can mediate the delivery of drug to the cells.

CONCLUSION
We have successfully functionalized GO and improved it dispersibility and biocompatibility. Functionalized GO was used to load and deliver poorly water soluble anticancer drugs. Hence, GO is considered as a promising material for drug delivery due to its non-toxicity and surface availability on both sides for drug loading.

REFERENCES

COLL 653

Functional hybrid materials by assembling metallo-biopolymers

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The central goal of this work was to construct a library of metal-biopolymer complexes that combine the rich information content of biopolymers with the tunable redox, magnetic, optical, and catalytic properties of metal-ligand units. Metals can be
incorporated into biopolymers by three different ways: tethering to the polymer backbone as a preformed complex (class I), coordination with a ligand-biopolymer conjugate via a “plug and play” approach (class II), or direct coordination with groups intrinsic to the biopolymer (class III). We have designed peptide-based biopolymers to pursue each possibility. Through comprehensive and systematic investigations, representatives of all these classes of metallo-biopolymers have been demonstrated. The successful introduction of metal-ligand components into specific polypeptide sites has been characterized by nuclear magnetic resonance, gel electrophoresis, X-ray photoelectron spectroscopy, scanning electron microscopy, and time-dependent monitoring of bioconjugation reactions using mass spectrometries. The resulting electronic/optical activities of metallo-biopolymer assemblies have also been studied by absorption/fluorescence spectroscopy and electrochemistry. The effort supports the development of technologies based on stimuli-adaptive (bio)materials with potential new applications in self-healing, molecular opto-electronics, and bio-sensing.

COLL 654

PolyGraphene muco-adhesive patches for sustained delivery of STAT-3 inhibitors for anti stem-like cell therapy

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Sustained release of drug formulations in buccal region of the oral cavity have been gaining popularity and medical acceptance worldwide. Major challenges for such patches are their biocompatibility, drug loading capacity, release efficiency, directionality of drug release and finally controlled time dependent biodegradation, which are yet to be handled efficiently.

At this very end, we have prepared a novel polymer-graphene (PolyGraphene) based drug loaded membrane and packed them in natural polysaccharide based patches for addressing the above mentioned points. Polycaprolactone (PCL) was melted and admixed with graphene nanoplatelets (GRNP) via hydro-thermo-evaporation method to prepare membranes in presence or absence of therapeutic agents. Niclosamide, a FDA-approved anthelmintic used in the treatment of worm infections was selected as the therapeutic agent. It is also a known inhibitor for cancer stem-like cells via STAT-3 (Signal Transducers and Activators of Transcription) inhibition pathway. Membrane loaded with niclosamide in PCL alone was prepared as control. These membranes were found to be more responsive in releasing the niclosamide at slightly acidic pH of 6.8 and time dependent manner where GRNP was the regulator of the drug release. These membranes were further tested for cell toxicity in representative human cell lines MD-MB231, MCF-7 and C32 cells by MTT and Trypan blue assays. Results indicated highly significant ability to inhibit the cell growth along with high percentage of cell death with niclosamide loaded patches. Agarose gel electrophoresis was able to confirm negligible
leaching of niclosamide in gel material. Detailed membrane engineering protocols, characterization and biological studies will be presented.

**COLL 655**

**Functionalized graphene aerogels**

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Aerogels have low density and high surface area, so they are ideal candidates for catalyst supports and sensors. Graphene oxide (GO) produced through oxidation of natural graphite can be dispersed in water, lyophilized and reduced to form electrically conductive reduced graphene oxide (rGO) aerogels with densities as low as 0.5 g/cm³ and surface areas near 1000 m²/g. The pore morphology is controlled by the direction of freezing those suspensions forming aligned, continuous ~20 µm pores, providing more active surface area relative to traditional mesoporous carbonaceous aerogels. Our group has found that with the use of chelating agents, metal ions can adsorb onto GO without precipitation, facilitating fabrication of metal salt-coated GO aerogels. The metal and GO can then be simultaneously reduced to form the metal nanoparticle-decorated rGO aerogels.

We found that the imparted functionality of metal nanoparticles can be done controllably, with variable nanoparticle surface density and size. Functionalized aerogels were found to be an active reversible hydrogen sensing material. The process was applied to several transition metals, and is also applicable to other systems to
produce novel catalyst composites. Currently we are investigating this novel material as Li ion battery electrodes, supercapacitor material and as a catalyst support.

 COLL 656

Surface reactivity of nanoporous ZIF-8 thin film toward energy-related gases

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Zeolitic imidazolate frameworks (ZIFs) have strong potential for numerous applications in energy-related gas storage, catalysis, and sensor development. Much of the work to this point has focused on the synthesis and investigation of the bulk properties of microcrystalline ZIFs. In this study, we focus on nanoporous ZIF-8 thin films supported on a Au substrate as many applications depend on the preparation of films. More importantly, the study of such films can provide fundamental insight into adsorption and reaction mechanisms. We used X-ray photoelectron spectroscopy (XPS) to determine the identity of the surface-terminating groups, the first groups encountered by any entering gases. In parallel, we investigated the adsorption of energy-related gases, including CO\textsubscript{2}, H\textsubscript{2}O, and methanol by ZIF-8 films using temperature programmed reaction spectroscopy (TPRS). By combining these techniques with quartz crystal microbalance (QCM) measurements of film mass, we were able to determine gas uptake of the films and compare these uptakes to bulk measurements. Under low-temperature, low-pressure conditions, we observed uptakes of CO\textsubscript{2} very similar to that of the bulk microcrystalline ZIF-8, while uptake of water is limited, likely due to hydrogen bonding interactions with external terminating surface groups. This work reveals a method which allows one to distinguish between species which occupy the pores of the film from those which reside at the surface, and demonstrates more generally the ability to monitor the interactions of gases with supported nanoporous materials in ultra-high vacuum, opening the door to understanding mechanisms of adsorption and reaction of gases of interest.

 COLL 657

Building well-organized 3D carbon nanomaterials

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Carbon nanomaterials such as graphenes and carbon nanotubes have attracted extensive attentions due to their excellent chemical and physical properties, e.g. high conductivity, high surface area, good corrosion resistance, and excellent temperature
stability. In recent years, building well-organized 3D carbon nanostructures based on chemically modified graphenes and carbon nanotubes holds great promise in new energy applications such as supercapacitor, lithium ion battery, and fuel cell. In this talk, we will present our recent research on the synthesis and characterization of the well-organized 3D carbon nanostructures via chemical modification and solution processing.

1Supported by the AFOSR-MURI (Grant AFOSR FA9550-12-1-0037)

COLL 658

Microencapsulation of hydrophobic liquids in closed all-silica colloidosomes

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In this work a facile approach for the microencapsulation of hydrophobic liquids in closed solid all-silica colloidosomes is reported. The method is based on the formation of oil-in-water emulsions stabilized by silica nanoparticles and subsequent gluing of the particles at the water/oil interface by a silica precursor polymer – hyperbranched polyethoxysiloxane. By this means different oils are successfully enclosed in hence formed all-silica colloidosomes with almost 100 % efficiency. Via a systematical study it is demonstrated that this process is a delicate interplay between the emulsion stability, oil polarity and sol-gel reaction kinetics. This approach allows fabricating microcapsules of hydrophobic liquid substances in a mechanically stable, chemically inert and biocompatible matrix, silica, with high encapsulation capacity and a controlled release profile, see.
Simple but precise engineering of functionalized nanocapsules through nanoprecipitation

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There has been a growing interest in the preparation of synthetic capsules owing to their numerous applications (pharmaceuticals, catalysis or imaging). Routes to polymeric colloids in the submicronic scale usually require soft matter technologies (self-organization of amphiphilic block copolymers, LbL deposition on sacrificial template particles, polymerization-induced self-assembly or interfacial polymerization in miniemulsion conditions).

Another means of generating nano-objects relies on the nanoprecipitation technique or “Ouzo effect”, the principle of which lies on the supersaturation of whatever hydrophobic solute (oil, polymer, solids) dissolved in a hydrophilic solvent (acetone, DMF…) by adding a far excess of the non-solvent, water. When conditions are set up in a narrow range of the ternary phase diagrams, one can reproducibly generate colloids.

Herein we present a general undemanding strategy to build multi-tagged, oil-filled nanocapsules with controlled morphologies. We show that the exploitation of phase diagrams for polymer/water/acetone and hexadecane/water/acetone systems allows to define experimental conditions in which polymer chains preferentially stick at the interface of the hexadecane droplets to generate polymeric nanocapsules. The resulting nanocapsules can be cross-linked, shell-functionalized with fluorescent tags or molecules of biological interest and/or loaded with actives in a rapid one-pot procedure.
Thermostimulable multi-core-shell capsules

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Wax@SiO₂ thermo-stimulable core shell particles

Encapsulation is widely used in very diverse applications, from drug delivery to carbon-free self-copying paper. Various techniques allow for a compound to be protected from its surroundings, and vice-versa, until delivery is needed. Encapsulation is also used to ensure a steady and slow delivery of a chemical, usually a drug.

Previous research led to an original synthetic pathway to prepare thermo-responsive capsules made of a wax core surrounded by a silica shell, allowing the delivery of the encapsulated compound in response to a temperature elevation¹.¹

The process is based on the elaboration of a wax in water emulsion above the wax melting temperature, using particles to stabilize the liquid wax droplets (Pickering emulsions). The use of silica nanoparticles allows a high droplets monodispersity thanks to the limited coalescence phenomenon and a direct control of the droplets' size by varying the nanoparticles/wax ratio.
The emulsion is then cooled down at room temperature, below the wax melting point, and the obtained wax crystals suspension is mineralized by the hydrolysis and condensation of a silica precursor at the wax-water interface.

Under heating, the inner wax expands and the shell breaks leading to the liquid oil release, as seen on fig.1. By an appropriate choice of the wax, the temperature of release can easily be tuned. Such capsules that allow triggered deliverance provoked by an external stimulus belong to the class of smart materials.

Figure 1 : Steps of wax liberation from a wax@SiO$_2$core shell particle under heating.

**Toward capsules complexification**

Even though the temperature-controlled release of the wax core otherwise encapsulated by the silica shell may lead to several applications on its own, its hydrophobic nature forbids the use of hydrophilic adjuvants.

To address that issue we propose two new synthetic pathways using the same concept, namely the use of wax expanding when melting and thus breaking the silica shell, applied to more complex emulsions.

We explored two different and complementary approaches: using a wax in water in oil double emulsion (fig. 2), and a water in wax in water double emulsion. The
mineralization process was very similar to the one used previously on the simple capsules.

Figure 2: wax@water@SiO$_2$ double capsule

We show that we obtain thermo-stimulable double capsules using both synthetic pathways, opening the way to the encapsulation of any type of adjuvant and its release at the desired temperature.$^{[2, 3]}$ The simple syntheses and the use of emulsions allow an easy scaling up of the processes.

Moreover, the demonstration that this concept works with double emulsions opens the path to the use of other multiple emulsions or of the millifluidic tool to increase the complexity of the thermo-stimulable capsules in order to use them in applications such as multi-therapy delivery.


Molecular-level characterization of anisotropic nanoparticles with NMR spectroscopy

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Anisotropic gold nanoparticles, such as “patchy” particles or nanorods, are challenging to characterize on the molecular level. Our group and others have functionalized gold nanorods with organic ligands, polymers, and biomolecules, but many applications require a thorough understanding of the surface morphology. For example, nanorods are passivated by a bilayer of cetyltrimethylammonium bromide (CTAB), but little is known about the packing density, degree of interdigitation, or other features that affect the rods' reactivity and stability. In this research, we use a series of one- and two-dimensional NMR techniques to decipher the ligand morphology of anisotropic gold particles.

Encoded cellular shapes for synthesis of non-spherical particles

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The success of living systems rests upon a mastery of molecular to micro-scale assemblies and materials. Multi-scale processes such as metabolism and cell communication rely on evolutionary optimized structures to dictate function where the common thread of asymmetry pervades key aspects of these systems. As these principles increasingly inform synthetic chemistry this is reflected, for instance, in recent aims of colloid chemistry where the development of asymmetric, anisotropic, patchy, Janus, and other non-spherical particles has gained substantial momentum and use across technological applications and fundamental studies of self-assembly and recognition. However, synthesis of non-spherical particles with prescribed shapes presents particular challenges given that bulk syntheses of colloidal-scale materials tend to produce spherical particles due to the dominance of viscous forces. This challenge has been addressed using a number of strategies, yet despite these achievements, we still cannot synthetically mirror the complexity and precise control over shape observed in cells and microorganisms. As an example, consider a mammalian erythrocyte (RBC) which displays concerted, mechanically-encoded shape changes in response to chemical perturbation—from cups and disks, to crenated and spherical bodies. An ability to translate these shapes into more durable/functional
materials would offer an entirely new paradigm for generating colloidal-scale, non-spherical particles.

Here we present a strategy to translate these cellular shapes into composite and inorganic particles. Using our recent technique for silica bioreplication (PNAS, 109:17336–17341), we show directed formation and capture of the stomatocyte-discocyte-echinocyte-spherocyte sequence of RBC shapes in silica, demonstrate retained activity and conversion to other functional materials (e.g. silicon, iron carbide), and show tunable bulk material properties based on particle-particle cohesion forces. This ability to employ the structural diversity of cells for particle synthesis provides new avenues to develop asymmetric particles, additives and bulk materials with the complexity and function of living systems.

COLL 663

Synthesis of magneto-responsive, hybrid, and Janus microrod particles

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Magnetic particles that can be remotely manipulated by an external magnetic field have attracted considerable interests for applications, including bioimaging, biosensing, multiplexed detection, and separation, transport, and sorting in microfluidic devices. While most studies have focused on spherical magnetic particles, it has been reported that magneto- and electro-rheological properties can be enhanced using anisotropic particles. Here, we report a facile and versatile method to fabricate monodispersed hybrid and Janus microrod particles of variable size and shape, and investigate their magneto-responsive behaviors in aqueous dispersions with and without geometric confinement. The key feature of our method involves co-assembly of silica colloidal particles and magnetic iron oxide nanoparticles in a poly(dimethylsiloxane) (PDMS) mold with a periodic micron-sized hole array, followed by infiltration and UV curing of epoxy resin to lock the particles, and releasing the microstructures from the mold and the substrate. The synthesized magnetic microrod particles were highly responsive: they could be isolated and flipped freely and reversibly. Further, our fabrication strategy allowed for creation of diblock and triblock-like Janus particles, where magneto-responsiveness and fluorescent emission could be integrated into different blocks within a single rod particle. Specifically, the use of silica particles in one of the blocks is advantageous since different functionality, surface chemistry, and fluorescent dyes can be introduced in addition in sequestering magnetic nanoparticle. Using these particles, we demonstrated field-responsive displays of multiple colors.

COLL 664

Pseudo-solid, shear-thinning gel formation in binary dispersions of metal oxide nanoparticles at low volume fractions
Metal oxide nanoparticles (np's) have direct application in the pharmaceutical, food, medicine, electrochemical and catalytic industries. Mixed metal oxide np's are known to form pseudo-solid shear thinning gels at low concentrations. The hydroxyl groups on the surface of the np's is known to form stable aqueous dispersions which of great importance for forming gel network systems. Fundamental characterization of such systems is imperative due to their application as viscosity adjusters, catalyst supports, fillers, pigments and more. This paper highlights the efforts underway at University of Oklahoma and Oklahoma State University in using transmission electron microscopy, small-angle x-ray scattering, and acoustic techniques for particle characterization for specific application in the catalytic and electrochemical industries. This work explores the morphology, particle size distribution, and stability of these systems at various pH's and solid concentrations. This work also utilizes several mixed metal oxide systems such as alumina, titania and silica and is coupled with optical techniques to characterize the gel network systems. The particle size measurements using various analytical techniques will lead to fundamental characterization of these complex systems that will lead to enhanced diffusional control in catalytic systems.

COLL 665

Assembly of 2D highly-ordered arrays of nanoparticle dimers directly on a substrate

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In order to incorporate nanostructures into functional devices, it is imperative to create an effective, reproducible, and economic method to manipulate the systematic arrangement of nanostructures patterning, alignment, and orientation on a substrate. Two dimensional array (2D) of metal nanoparticles (MNPs) are of great interest in the field of energy, optoelectronics, and biosensing because of their intrinsic optical properties such as localized surface plasmon resonance. Top-down techniques such as electron beam lithography and vapor deposition are commonly used to fabricate highly ordered 2D array of MNPs. Though these techniques offer superior flexibility and precision in arranging MNPs directly on a substrate, they are complex and expensive.

We developed a method to fabricate highly ordered 2D arrays of dimers of MNPs with different compositions, sizes, and shapes directly on a substrate in a controlled manner. This method involves i) the assembly of MNPs into 2D array with hexagonal packing directly on a substrate via solvent evaporation process, ii) the selective removal of thiol
ligands from the top surface of MNPs by selective etching process without deteriorating the 2D array, and iii) the subsequent assembly of other MNPs on top of the 2D array through functional linkers or electrostatic interactions. MNPs with different sizes can be readily integrated into the arrays to produce dimers with controlled symmetry. The distance between dimer islands can be precisely controlled by tuning the ligands on the MNP surface. This is a simple, and low-cost, general method for generating high-quality arrays without the need of sophisticated and expensive instruments. Scanning electron microscopy and atomic force microscopy were used to study the morphology of the nanostructures as well as the topology of the 2D array of MNP dimers. This highly ordered array of dimers may find applications in surface-enhanced Raman scattering signal detection, photovoltaic devices, and photonic crystals.

COLL 666

Studies on encapsulation, functionalization, and applications of liquid marbles and dry liquids

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Studies on liquid marble encapsulation via vapor phase deposition and polymerization of ethyl-cyanoacrylate (superglue monomer) as well as on incorporating photoresponse to liquid marbles will be described. Further, the use of microscopic liquid marbles (dry liquids) for gas purification will also be discussed.

COLL 667

Hollow nanocages dispersion and its photothermal properties

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The bimetallic Au and Ag alloyed nanocages, and Ag and Au core-shell structure, and Au-pitted silver nanocubes had been studied in different surrounding mediums, such as liquid and polymer matrix. The DDA simulation found to be a powerful tool to characterize a colloidal dispersion of the plasmonic nanoparticles. The effect of the medium around the cages on the surface plasmon resonance spectra (SPR) had been suggested based on the DDA simulations. The photothermal response strongly relies on the optical properties and plasmonic peak position. The highest photothermal response was observed at wavelength close to the plasmonic peak. Such sensitivitity could be potentially sufficient for fabrication photothermal detectors.
Polymeric micelles assembly for the preparation of large sized mesoporous TiO$_2$

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The micelles of triblock copolymer poly(styrene-$b$-2-vinyl pyridine-$b$-ethylene oxide) (PS-$b$-PVP-$b$-PEO) are used for the synthesis of large sized mesoporous TiO$_2$. The three different blocks in the obtained stable micelles each contribute towards the formation of the targeted mesoporous materials. The hydrophobic PS block stabilizes the micelles and controls the pore size of mesostructure. The strong interaction of titanium tetraisopropoxide with the PVP shell enables fabrication of highly robust walls and the hydrophilic PEO helps orderly packing of the micelles during solvent evaporation. The wall thickness and pore size can be easily tuned by changing either molecular weight of polymer or solution properties. This approach is based on assembly of the stable micelles using a simple, highly reproducible method and is widely applicable towards numerous compositions that are difficult for the formation of mesoporous structures.

Hydrosilylation kinetics of silicon nanocrystals: Microwave vs. thermal

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Silicon nanocrystals (ncSi) below 5 nm in diameter, the exciton size of bulk silicon, exhibit size-dependent photoluminescence (PL) that arises from quantum confinement effects. The chemical, physical and biological properties of nanomaterials like ncSi are not just controlled by size and shape but also by organic molecules that have been chemically anchored to their surfaces, which play a central role in determining the function and utility of nanomaterials. Specifically, ncSi in this size range can be made colloidaly stable by functionalizing the surface with covalently bound organic molecules through hydrosilylation of surface silicon hydride bonds with a terminal alkene, an attribute which is beneficial for solution processing of nanocrystal silicon devices. In organic synthesis, microwave heating instead of traditional oil bath heating has often been reported to enhance the rate of chemical reactions. While the kinetics and mechanism of hydrosilylation of silicon wafers and porous silicon have been reported, no quantitative study of ncSi exists in the literature, and neither does direct comparison between the microwave hydrosilylation and oil-bath hydrosilylation. Here we report the hydrosilylation kinetics of hydride-capped ncSi with 1-decene in a microwave reactor compared to a thermal reactor for the first time. It is found that microwave heating has no evident acceleration effect on the hydrosilylation rate relative to conventional thermal heating, suggesting that the reaction mechanism is the same for both methods and the reaction extent would only depend on the temperature and time.
Colloidal ZnO/Cu hybrid nanocatalysts for CO₂ hydrogenation to methanol

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The conversion of the CO₂ to methanol is highly desirable and shows great promise as a sustainable source of liquid fuel as well as a precursor for a range of commodities.

Colloidal Cu(0)/ZnO hybrid nanoparticle catalysts have been developed for the hydrogenation of CO₂ to methanol. Well-defined ZnO nanoparticles, surface ligated with organic groups (carboxylate/phosphinate) were prepared via an efficient hydrolysis route, without the need for excess surfactant or size-selection steps. The resulting 3-4 nm particles have a narrow size distribution and are soluble in organic solvents.¹

Using various copper precursors and reduction conditions, copper nanoparticles have been formed on the ZnO surface to give a highly active catalytic system, reducing CO₂ to methanol (CO₂:H₂ 1:3, 50 bar, 523 K, squalane) with over triple the activity of a reference commercial ternary catalyst (Cu/ZnO/Al₂O₃).²

Adjusting the copper loading affects the morphology of the catalyst particles with a corresponding change in the catalyst activity. The ligands on the catalyst surface can be tuned to control the stability of the catalyst.


Kinetic study for the oxidation caused by aqueous nano-C₆₀ aggregates

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With the multi ton production of fullerene (C₆₀) in industry due to its wide spread applications and commercialization, the concern of the biological and environmental effects of this compound has significantly increased. The ability to form stable aqueous C₆₀ colloids (known as nano-C₆₀ or nC₆₀) and the availability of these in natural systems at environmentally-relevant concentrations led to the studies of its toxicity. In this
research oxidation caused by fullerene colloidal suspensions is investigated by fluorescent assays to monitor oxidation with the probe molecule dihydrodorhodamine-123 (DHR123). Presence of C_{60}O in these colloidal suspensions considered to have increased ability of oxidation. To better understand the behavior of the probe molecule, calibration studies with common oxidants such as hydrogen peroxide (H_2O_2), ferric chloride (FeCl_3) and potassium permanganate (KMnO_4) were investigated. Method of initial rates was used to propose the rate equation for the oxidation observed.

COLL 672

Characterization of iridium oxide nanoparticles (IrO_x NPs) for use as a water oxidation catalyst

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Solar generation of fuels is an attractive alternative to more commonly used non-renewable fuel sources due to the amount of energy reaching the earth’s surface from the sun at any given time. One proposed method of achieving this is the Dye-Sensitized Photoelectrosynthesis Cell (DSPEC), which involves a chromophore-catalyst assembly to store the energy from sunlight into common fuels, such as H_2, CH_3OH or CH_4. A common hurdle for these cells is the large kinetic barrier of water oxidation on the anode half of the cell, which requires a catalyst to proceed. Small iridium oxide nanoparticles (< 2 nm in diameter) have proven to be an effective catalyst for water oxidation across a wide range of pH. However, little is known about why they are such good catalysts. The research presented aims to characterize and more fully understand the makeup and reactivity of IrO_x NPs using various electrochemical, microscopic and spectroscopic techniques. Further knowledge of the composition and surface chemistry of the IrO_x NPs and their reactivity will aid in the development of more efficient solar fuel cells.

COLL 673

Small clustered water for effective hydrolysis of triglyceride

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Our body digests fat by hydrolysis with both enzyme lipase and surfactant bile acids. We focus on the nature of water as a key reactant. In general, oil does not mix with water. However, a natural alkaline water having very small clusters can mix with triglyceride well and also forms an emulsified interfacial phase. This state enhances hydrolysis of triglyceride. Significant increase in reaction rate occurred with lipase alone and without the presence of bile acids as followed by infrared spectroscopy. In contrast, regular water with typically larger cluster size did not mix well with triglyceride and could
not offer the enhancement. The surface tension is much lower than that for regular water and interestingly it is close to that for oily triglyceride. Reasons for the enhancement are explained along with eliminated anomalies. It is believed that the effect at least in part is due to the smallness of water which increases reaction probability. These results are encouraging for people with insufficient secretion of bile acids that prevents them from eating fat due to liver or gallbladder problems as well as for providing new means to enhance fat digestion. Our results suggest that the physical characteristics of water can positively influence the digestive process. Research focused on water properties in human body reactions is rare and to our knowledge none for the reaction studied here. This kind of research is expected to create new directions in physiological science and related fields in medicinal sciences when we consider the numerous important chemical reactions in human body that involves water.

COLL 674

Optical printing of electrodynamically coupled metallic nanoparticle chains

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Optical forces are being used with increasing frequency to immobilize nanomaterials on substrates with desired configurations and patterns. It is a contact-less tool so there is little to no physical damage to samples. In this poster, we present an efficient approach to deposit electrodynamically coupled metallic nanoparticle arrays on chemically modified substrates by a combination of optical trapping and electrodynamic inter-particle forces for spatial guidance. Chemically tuning the nanoparticle-surface interactions to be appropriately repulsive to spontaneous deposition allows the optical trapping forces to be the sole determinant of deposition. The deposited patterns show preferred separations between nanoparticles when positioning the optical line trap with various inter-column separations. Overall, the findings suggest a meso-scale interaction attributed to optical field-induced optical binding forces. Electrodynamics simulations of the inter-particle interactions corroborate optical binding as accounting for our experimental results. This “optical printing” method is a promising approach to effectively fabricate dense nanoparticle arrays on meso-scales with nanoscale positional precision.

COLL 675

From ordered mesoporous materials to single-micelle-templated nanoparticles

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The surfactant micelle templating approach, which is known from its power and versatility in the synthesis of ordered mesoporous solids templated by periodic arrays of micelles, has recently emerged as an avenue to well-defined single-micelle-templated nanoparticles with spherical or tubular voids. It is important to understand what conditions trigger the formation of the single-micelle-templated nanoparticles so that these exciting and practically useful nanoscale structures could be synthesized in a predictable manner. We have shown that the lowering of the ratio of the framework (organosilica or silica) precursor to the surfactant under conditions otherwise favorable for the formation of ordered mesoporous materials often (but not always) renders nanoparticles having single spherical or tubular voids. The strategy is discussed for Pluronic (PEO-PPO-PEO) triblock copolymer surfactants and various organosilica and silica frameworks. The issues of the particle aggregation and the adjustment of the pore diameter and pore accessibility will be discussed.

COLL 676

Morphologies of cerium oxide as palladium nanoparticles support for heterogeneous catalysis

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Novel metal nanoparticles have been widely used as heterogeneous catalysts. However, due to their high surface area, they need to be stabilised to prevent them from agglomerating and maintain their small sizes. One method is to deposit them on high surface area metal oxides as metal nanoparticles support. Other than providing support, these metal oxides may influence the chemical properties of the nanoparticles, also known as metal-support interaction. This can be observed with cerium oxide supports\(^1\), although the fundamentals of this relationship are not thoroughly understood.

This project is aimed at investigating the variation of metal-support interaction by changing the morphologies of the cerium oxide support. Altering the morphology allows for tuning the exposed crystal planes\(^2\). In this study, different morphologies of cerium oxide were synthesised and characterised. They were then loaded with Pd nanoparticles and their heterogeneous catalytic behaviour was compared. By complimenting these catalytic results with other analytical techniques such as temperature programmed reduction (TPR) and X-ray Photoelectron Spectroscopy (XPS), the role of CeO\(_2\) as a metal nanoparticle support would be more fundamentally comprehended.

COLL 677

Monolayer assembly of ferrimagnetic Co\(_x\)Fe\(_{3-x}\)O\(_4\) nanocubes for magnetic recording
Synthesis and self-assembly of ferromagnetic/ferrimagnetic nanoparticles are important for magnetic data storage application in hard disk drive and magnetic tape. In order to get high density data storage, uniform size and shape of the nano-building blocks are needed. As an important ferrimagnetic material, cobalt ferrite (CoFe$_2$O$_4$) shows very high magnetic anisotropy and coercivity, which is a desirable system for this application. Here I will discuss a facile synthesis of monodisperse Co$_x$Fe$_{3-x}$O$_4$ nanocubes through thermal decomposition of Fe(acac)$_3$ and Co(acac)$_2$. The magnetic properties can be easily tuned by controlling the size of the cube and composition of Co in cobalt ferrite. Using the self-assembly process, large-area monolayer assembly of the nanocubes is fabricated, which shows great potential as magnetic recording medium for data storage applications.

**COLL 678**  

**Novel membranes for adenovirus recovery from water**

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Prevention of waterborne disease outbreaks relies on the efficient detection of pathogens in drinking and recreational water. Development of sample concentration technology that ensures fast and high recovery of pathogens from aquatic samples is crucial for reliable detection. EPA-approved method VIRADEL (VIRus ADSorption and Elution) is expensive, exhibits low and poorly reproducible recoveries for certain viruses such as adenoviruses. Crossflow ultrafiltration (UF) is an emerging alternative method of waterborne pathogen concentration. The membrane with an appropriate pore size can simultaneously concentrate a wide range of microbial pathogens without concentrating molecular toxins and low molecular weight qPCR inhibitors. To decrease virus adhesion to the membrane, UF membranes are coated with calf serum. In contrast to VIRADEL, UF technique exhibits significantly higher recovery for some viruses. However, overnight deposition of calf serum on UF membranes is a poorly controlled and time consuming process. Such protein coating is also prone to contamination during transport and under field sampling conditions.

To overcome this limitation, we propose a conceptually novel approach to virus concentration based on sacrificial membrane films. Such films can be prepared by coating an ultrafiltration membrane with a polyelectrolyte multilayer (PEM) using layer-by-layer adsorption of polycations and polyanions. Main advantages of the proposed
approach are (1) fast and reproducible preparation of membranes (less than 1 hour), (2) highly controllable properties (charge, hydrophilicity, swellability, etc) resulting in a highly anti-adhesive membrane surface, (3) dissolution of coatings to recover any virus that is adsorbed on the film.

We designed anti-adhesive sacrificial membrane films by coating polyethersulfone membrane with a PEM consisting of alternating layers of chitosan and heparin and assessed the effectiveness of the coated membrane in recovering human adenovirus 40 (HAdV 40), a non-enveloped, double stranded DNA virus that is responsible for most cases of adenovirus-associated gastroenteritis. We also comparatively evaluated the recovery of such virus by traditional calf serum blocked membrane. To our knowledge, this is the first study that evaluates both of these approaches for HAdV recovery from water. Our results demonstrate that coating a membrane with a PEM film results in very high pre-elution recovery from DI water (∼90%). HAdV 40 recovery from surface water is ∼60 % for both PEM-coated and calf serum-blocked membranes.

COLL 679

Antifungal activity and mechanism of palladium-modified nitrogen-doped titanium oxide nanoparticle photocatalyst on agricultural pathogenic fungi *Fusarium graminearum*

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As a common plant disease, *Fusarium* head blight (FHB) is one of the devastating diseases on small grain cereal crops, which could significantly reduce grain quality and yield. FHB could also produce a variety of mycotoxins which are detrimental to livestock and pose a potential safety concern to human foods. *Fusarium graminearum* is the pathogen for FHB on wheat. The macroconidia formed by *F. graminearum* plays an important role in the dissemination of FHB. The conventional fungicidal methods rely heavily on synthetic chemical pesticides. However, synthetic chemical pesticides are usually hazardous to animals and the environment due to their residual toxicity. Furthermore, fungi have developed resistance to some traditional fungicides, such as benzimidazoles and dicarboximides, which makes it more difficult to control fungal growth. Thus, alternative antifungal approaches need to be developed, which should overcome the fungicide resistance for a better fungicidal effect while posing no harmful effect on the environment. It would be even better if it could also decompose mycotoxins produced by fungi.

As an environmentally friendly alternative to the commonly used chemical fungicides, a highly effective photocatalytic disinfection of *F. graminearum* macroconidia under visible
light illumination was demonstrated on a visible-light-activated palladium-modified nitrogen-doped titanium oxide (TiON/PdO) nanoparticle photocatalyst. Because of the opposite surface charges of the TiON/PdO nanoparticles and the *F. graminearum* macroconidium, the nanoparticles were strongly adsorbed onto the macroconidium surface, which is beneficial to the photocatalytic disinfection of these macroconidia. The photocatalytic disinfection mechanism of TiON/PdO nanoparticles on these macroconidia could be attributed to their cell wall/membrane damage caused by the attack from ROSs as demonstrated by the fluorescence/phase contrast microscopy observations, while a breakage of their cell structure was not necessary for their loss of viability.

**COLL 680**

**Antibacterial activity and cytotoxicity test of multi-walled carbon nanotubes decorated with silver nanoparticles**

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Recently, various nano-scale materials including silver nanoparticles have actively been studied for their effective prevention of bacterial growth. It is important to enhance antibacterial properties of nanomaterials while maintaining their biocompatible characteristics. Engineering of nanostructures by conjugating different dimensional (nanodots and nanotubes, for example) may help keeping nanomaterials' safety and increasing their target-specific bacterial mortality. Multi-walled carbon nanotubes (MWCNTs) were treated with acids in several steps to decorate them with silver (Ag) nanoparticles. Chemical reduction of Ag cations by ethanol solution on the acid treated MWCNTs produced nanoparticles around the nanotubes [1]. The synthesized complexes, Ag-MWCNTs, were characterized by transmission electron microscopy (TEM), X-ray diffractometry (XRD), energy-dispersive X-ray (EDS) and evaluated for their antibacterial function against Methylobacterium and Sphingomonas. The biocompatibility of Ag-MWCNTs co-cultured with human peripheral mononuclear cells was measured by the MTT assay.

In sum, the minimum amount of Ag-MWCNTs effectively killing the bacteria was assessed and that concentration showed no harmful influences on the human cells.

**COLL 681**

**Multilayer nanofilms onto curved objects for biomedical opportunities**

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**INTRODUCTION**

Nano-film offers various opportunities to give an additional desired functions to
biomedical objects with a nanometer scale control over the thickness and composition as previously reported.\(^1\)-\(^3\) Various materials ranging from polyelectrolytes to nanoparticles, collagen, and RNA could be incorporated with the nano-films through the various complementary physical interactions (i.e., hydrophobic interaction, hydrogen bonding, electrostatic).\(^4\)-\(^6\) Moreover, nano-film enables preparation of multilayer structures onto almost any kinds of substrate, regardless of its shape and size.\(^7\)-\(^9\) In this presentation we presents the simple methods to prepare functionalized nano-films onto curved surfaces such as colloidal particle, hydrogel, and stem cells. The building block of nano-film can be not only polymers but also functional materials such as protein, nanoparticle, graphene and so on. For example, hollow graphene capsules prepared through Layer-by-Layer (LbL) assembly of the oppositely charged stable reduced graphene oxide (rGO) nanosheets onto a sacrificial polystyrene (PS) colloid template and block copolymer micelles (BCMs)-multilayer coated colloidal particles for drug delivery.\(^10\)-\(^16\)

**EXPERIMENTAL**

Preparation of Hollow Capsules of reduced graphene oxide (rGO) nanosheets assembled on a sacrificial colloidal particle. Preparation of the (rGO-NH\(^3\+)/rGO-COO-) multilayer-coated polystyrene colloids: Negatively charged polystyrene colloids was deluted with deionized water. Subsequently, a suspension of rGO-NH\(^3\+\) (pH6) was added. After deposition for 10 min with a mild vortex, the excess rGO-NH\(^3\+) were removed by three centrifugation (8,000 rpm, 4 C, 5 min). rGO-COO- (pH6) was then allowed to deposit successive layer onto the rGO-NH\(^3\+\)-coated PS colloids under same conditions. The above process was repeated until 3 bilayers of (rGO-NH\(^3\+)/rGO-COO-)\(^3\) have been fabricated onto PS colloid template.\(^16\)

Preparation of Tunable Superhydrophobic and Optical Properties of Colloidal Films Coated with Block Copolymer Micelles (BCM)/BCM multilayers. Preparation of BCM multilayer films: The concentration of the BCM solutions and Poly(styrene-block-4-vinylpyridine)(PS-b-P4VP)/Poly(styrene-block-acrylic acid) (PS-b-PAA) multilayer-coated silica colloids used in all the experiments were prepared according to previously reported. Negatively charged 600nm silica colloids was diluted with deionized water. Subsequently, PS-b-P4VP was added. After deposition for 10 min, the excess PS-b-P4VP BCMs were removed by three times centrifugation. PS-b-PAA was then deposited onto the PS-b-P4VP-coated silica colloids under the same conditions. The above process was repeated until 3 bilayers of PS-b-P4VP/PS-b-PAA were deposited onto the silica nanoparticle.\(^10\)

**RESULT AND DISCUSSION**

Layer-by-Layer (LbL) assembly is a versatile film fabrication method to deposit functionalized and nanoscaled multilayers onto substrate. Various interactions including electrostatic interaction, hydrophobic interaction, and hydrogen bonding can be adopted for LbL assembly. Not only flat surfaces but also curved surfaces are candidates for substrates of LbL assembly. For examples, functionalized multilayer thin films could be
deposited onto colloidal nanoparticles, cells, and hydrogel. And also there are a variety of materials that can be deposited by LbL assembly including polyelectrolyte, graphene oxide, RNA, and collagen.

Figure 1. Schematic illustration of LbL assemblies which can be applied to various curved surface.

Take full advantages of LbL assembly, we could prepare hollow graphene capsules based on the electrostatic interactions by repeatedly depositing the suspensions of rGO-COO- and rGO-NH3+ onto a colloidal PS particle to afford the multilayer in the architecture of \((\text{rGO-NH3+/rGO-COO-})_n\) \(n = \text{number of bilayers}\). After LbL deposition, as demonstrated with other previous reports of using sacrificial template to prepare the hollow nanostructure, hollow capsules composed of rGO sheet-paired multilayers were recovered by removing the PS colloidal template with selective solvent exposure. These hollow structures made by LbL assembly can incorporate therapeutics and used for targeting container.

In addition, spherical nanoparticles could be deposited on to surface of colloidal particle. The polymeric nanoparticle BCM is broadly used for drug delivery system with possibility of drug encapsulation. The BCM multilayers have been assembled onto colloidal silica surfaces via hydrogen-bonding and electrostatic interactions between complementary BCMs, anionic PS-b-PAA and cationic PS-b-P4VP. The nanostructured surface morphology of BCM multilayers onto colloidal silica template has been controlled by
varying either the charge density of hydrophilic BCM coronas (i.e., PAA or P4VP) or the molecular weight of the hydrophilic corona blocks and hydrophobic core (PS).

Figure 2. SEM images of silica colloids coated with BCMs. (Reprinted with permission from Hong et al. 2007; Copyright © 2007 Wiley)

CONCLUSIONS

In conclusion, nanofilms prepared from LbL assembly can offer opportunities to prepare desired multilayer thin films onto various curved surfaces with nano size thickness control. We could use almost any kinds of functional materials ranging from biologically active objects to inorganic particles as building block of nano-film onto curved surfaces.

REFERENCES

Pore formation in DMPC bilayers and *Listeria monocytogenes* by antimicrobial peptide melittin

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Antimicrobial peptides (AMP) kill microbial cells through insertion and damage/permeabilization of the cytoplasmic membranes. Since their mechanism of action differs from that of antibiotics, they could be very useful for combating drug resistant microbes and for treatment of microbial infections. Pore formation in DMPC bilayers by antimicrobial peptide melittin was monitored by leakage of fluorescent dyes (calcein, FD4 and FD20) of different molecular weights encapsulated within liposomes which indicated a lagtime which was larger for smaller melittin/liposome ratio and larger molecular weight of dye. In the second part of this study, the antimicrobial activity of native melittin against Gram positive bacteria *Listeria monocytogenes* was characterized by absorbance and plate count which also indicated a lagtime for deactivation that was concentration dependent. Mathematical models for the prediction of minimum inhibitory concentration as well as time of pore formation were proposed. Model predictions were compared with experimental data.

COLL 683

Engineering nanoparticle antitoxins utilizing aromatic interactions

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Methicillin resistant Staphylococcus aureus (MRSA) is a highly virulent pathogen capable of inflicting severe infections. This pathogen has a long history of developing resistance to antibacterial drugs, and many phenotypes are capable of immobilizing the host immune response by releasing peptide and protein toxins with the capacity to lyse human polymorphonuclear neutrophils (PMNs). The peptide phenol-soluble modulin α3 (PSMα3) has been identified as an important toxin released by the most virulent strains of MRSA. A library of colloidal polymer nonaparticles (NPs) was synthesized by precipitation polymerization to act as synthetic inhibitors of this toxin. The monomers incorporated into the polymers were chosen to compliment the functional groups of PSMα3 and generate a high affinity. We determined that aromatic monomers provided an enhanced affinity for PSMα3 and were effective at neutralizing the toxin in vitro. Our results indicate that aromatic monomers may be useful in engineering affinity between synthetic NPs and biomacromolecules.

COLL 684

Fabrication of self-sterilizing surfaces by covalently grafting cationic amphiphilic polymers

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Proliferation of multi-drug resistant bacteria (superbugs) on medical devices and surfaces accounts for the majority of hospital acquired bacterial infections. Thus, self-sterilizing surfaces with antibacterial properties are extremely desired in health care settings. Natural antimicrobial Peptide mimetic synthetic amphiphilic polymers having cationic charge and hydrophobic groups are known to disrupt bacterial cell membrane through columbic and lipophilic interactions. Highly retarded or improbable development of bacterial resistance toward cationic amphiphilic polymers has established them as an attractive candidate for antibacterial applications. Here we report the grafting of a 6-carbon spacer arm cationic amphiphilic polyacrylate on the glass surface to generate polymer coatings with antibacterial activity. The amphiphilcity of polymer was optimized by quaternization of tertiary amine with various lengths of alkyl groups. Scanning electron microscopy analysis and time-kill studies confirmed the membrane disruption mechanism of antibacterial activity.

COLL 685

X-ray diffraction of metastable crystal forms within picogram dots

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Experimental measurements of the earliest stages of crystal formation suggest rapid transitioning through metastable crystal forms before ultimately producing the most thermodynamically stable crystal form, supporting a >100 year old theory by Wilhelm Ostwald that has historically been challenging to test. Advances in measurement capability are described from coupling the second harmonic generation (SHG) microscopy directly into a beamline for synchrotron X-ray diffraction. The regions of interest identified by SHG microscopy were targeted for X-ray diffraction, enabling structural analysis of pg quantities of crystalline material. By confining crystallization to small volumes, inkjet printing places crystallization under kinetic control. As such, metastable crystals forms that would otherwise transition to stable forms could be kinetically trapped to provide snapshots of structures present during the early stages of crystallization. When inkjet printing racemic amino acid solutions, the XRD measurements confirmed spontaneous resolution of the crystal forms into separate homochiral crystals when crystallization was performed under kinetic control through inkjet printing. These results may allow for new, efficient routes for chiral resolution in chemical syntheses, and could provide insights into possible mechanisms for the amplification of amino acid homochirality in pre-biotic Earth.
Novel peptoid nanosheet assembly at the oil-water interface

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Peptoid nanosheets are a modifiable class of polymer that can accommodate side chain ligands via attachment to the nitrogen of the peptoid backbone. The interchangeability of the peptoid functional groups make them suitable for a wide range of temperature and pH conditions. Bilayers of peptoids form through an intermediate monolayer resulting in highly organized 2D nanosheets. Understanding the processes that mediate interfacial adsorption and assembly of nanosheets at the oil-water interface expands the diversity of applications including catalysts, molecular sensors, and artificial membranes by permitting oil soluble chemical reagents, minimizing evaporation of the aqueous phase, and allowing microfluidic production. The formation of peptoid nanosheets at the carbon tetrachloride-water (CCl₄-H₂O) interface was investigated by total internal reflection (TIR) vibrational sum frequency (VSF) spectroscopy and tensiometry measurements, helping to identify the molecular orientations and intermolecular forces involved in the packing of peptoid chains containing a variety of charge and steric...
groups, as well as showing that interfacial chemistry plays a key role in the sequence design and 2D assembly.

**COLL 687**

**Nanoparticle interactions with supported lipid bilayers studied by nonlinear optics**

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As part of a broad research effort in the NSF-funded Center for Chemical Innovation on Sustainable Nanotechnology, the goal of this work is to understand the fundamental chemistry of how nanoparticles interact with biologically relevant interfaces in situ at the molecular level. Surface specific nonlinear optical spectroscopies, namely second harmonic (SHG) and sum frequency generation (SFG), are used to investigate the interactions of nanoparticles with lipid bilayers as model cell membranes. Specifically, SHG allows us to probe binding interactions, while SFG allows us to investigate the effect of nanoparticle interactions with the molecular structure of the lipids.

We use resonant and nonresonant SHG to quantify interfacial charge densities and potentials in real time for bilayers of various lipid compositions with and without gold nanoparticles present. We have shown how a supported lipid bilayer carrying a negative interfacial potential may interact with positively charged as well as negatively charged gold nanoparticles. For the case where the interaction does not seem favorable based on electrostatics, charge-charge repulsion does not appear to inhibit particle-bilayer interactions. Combining this knowledge with the SFG results detailing the molecular structural changes due to the nanoparticle-membrane interaction, allows us to predict possible pathways for the molecular level nanoparticle-lipid bilayer interactions.

The impact of lipid composition, NP core composition, and capping ligand on the nanoparticle-membrane interactions is investigated. Understanding how nanomaterials interact with lipid bilayers at the molecular level is important for predicting and controlling molecular interactions of nanomaterials with living systems as well as designing environmentally and biologically sustainable nanomaterials.

**COLL 688**
Electric double layer formation: A molecular level study

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The molecular ionic surface structure and charge of the electric double layer around a nanodroplet and its structural change induced by hydrophobic effects are measured using vibrational coherent surface scattering spectroscopy, second harmonic scattering, and electrokinetic mobility measurements. Tetraalkylammonium chloride salts were added to negatively charged nanoscopic oil droplets in water. Upon varying the alkyl chain length of the cation from methyl to butyl, both the size of the cation and its hydrophobic interaction are increased. We find that tetramethylammonium ions change the electrokinetic potential and the water structure but do not detectably adsorb to the interface. Tetrapropylammonium and tetrabutylammonium ions clearly adsorb to the interface. The corresponding (Stern) layer appears to be a mixed monolayer of anions and cations. An estimate of the amount of cations in the Stern layer is also made.

COLL 689

NMR studies of functionalized mesoporous silica nanomaterials in aqueous solution

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Mesoporous silica nanoparticles are porous nanomaterials that have two dimensions on the nanoscale, the pore size and the particle size. Many potential applications for mesoporous silica nanomaterials are being investigated including heterogeneous catalysis, adsorption of environmental contaminants and biomedical imaging and drug delivery. Mesoporous silica has either highly ordered pores such as those found in MCM-41 and SBA-15 or less-ordered pores such as raspberry or worm-like forms. Mesoporous silica typically has nanometer size pores resulting in very high surface areas. The silanol surface surface groups on mesoporous silica can be chemically modified to tailor the surface characteristics, such as hydrophobicity/hydrophilicity, surface charge and/or biocompatibility for specific applications. For aqueous phase applications of mesoporous silica nanomaterials, it is critical to understand the molecular level interactions at the nanoparticle/water interface. The interactions of the surface functional group with interfaces of either water or water with environmental contaminants present were investigated using NMR techniques. Proton solution NMR experiments were performed including one and two-dimensional experiments, such as Diffusion Ordered Spectroscopy (DOSY) and Nuclear Overhauser Enhancement Spectroscopy (NOESY). The solution NMR methods described here provide critically important molecular level details about surface functional groups in aqueous solution.

COLL 690

Correlation of hard and soft protein corona for sugar-based nanocapsules
Nanomaterials, which come into contact with blood, are immediately covered with blood plasma proteins. Those proteins form the so called hard and soft protein corona, which relates to their respective binding affinities and exchange rates. While there is a lot of research focusing on the characterization of the hard protein corona, the soft protein corona is only barely understood as it can be only identified with methods like dynamic light scattering (DLS) or isothermal titration calorimetry (ITC), that require no extraction from the interaction medium. By a combination of different techniques we were able to combine hard and soft corona characteristics and to distinguish between hard and soft corona proteins.

We investigated the adsorption of plasma proteins onto differently functionalized hydroxyethyl-starch nanocapsules as well as the interaction with single proteins (human serum albumin (HSA), apolipoprotein A1 (ApoA1)). We applied SDS-PAGE and a protein assay to characterize the hard corona. The protein pattern and adsorbed protein amounts of the hard corona did not change significantly for all types of capsules. Further, ITC and DLS were applied to analyze the soft protein corona. ITC revealed that several thousand plasma proteins are loosely associated with all capsules after adsorption, leading to an increase of the hydrodynamic radius of 80-100 nm. The investigated processes are all enthalpy driven and indicate only weak interactions. Whereas the interaction of HSA with all capsules is similar to the plasma mixture, ApoA1 behaves very different. The binding affinity for ApoA1 is around 40 times higher than for HSA, but surprisingly only about 10 molecules are adsorbed to the surface. DLS measurements confirmed aggregates with increased size for HSA but not for ApoA1 adsorption. Additionally NH₂-functionalized capsules produced a strong endothermic reaction with ApoA1 along with a large entropy increase, most likely arising from a structure change upon adsorption.
implications of highly anisotropic metallic nanoparticles. Within recent decade, new applications have been developed for highly anisotropic gold nanoparticles (i.e. rods and wires) due to their high intensity of surface plasmon resonance at the tips. This characteristic makes these elongated shaped gold nanoparticles good candidates as biosensor, contaminant sensor, imaging contrast, or in drug delivery, and thermal cancer therapy. Shape, aspect ratio, and coating material effects on fate and transport of metallic nanoparticles especially gold within environment is the missing piece of this puzzle. In this research we tried to evaluate these parameters while mimicking real environmental conditions. We investigated gold nanorods with different characteristics such as aspect ratio and surface coating in various ionic strength solutions. Gold nanorods have been synthesized applying well-established methods and the surface coatings of nanoparticles have been changed as targeted. Different ionic strength solutions from very soft to very hard have been prepared according to EPA standards. Additionally effect of each salt such as CaSO₄ and MgSO₄ has been probed separately. The suspension and aggregates have been characterized by UV-VIS absorbance, DLS (dynamic light scattering), SEM (scanning electron microscopy), and TEM (transmission electron microscopy) techniques. Corresponding aggregation rate and aggregation assembly type (end-to-end or side-by-side) has been derived for each set of experiment by analyzing UV-VIS absorbance graphs. Results suggest that where the charge repulsion is the dominant mechanism for anti-aggregation, colloidal stability of nanoparticles dramatically reduces as the ionic strength of the solution increases. On the other hand, where steric barrier is the case, stability is almost independent of solution ionic strength.

COLL 692

Tribology in the space environment

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Multiple moving mechanical assemblies (MMAs) are required for the successful operation of virtually all satellites and launch vehicles. The correct choice of lubricants and tribocoatings is critical for the operation of spacecraft MMAs. However, the space environment is especially challenging. Examples include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. As such, they must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. A small number of liquid lubricants meet the vapor pressure requirement – while also meeting performance requirements for spacecraft applications – including synthetic hydrocarbons and perfluorinated polyalkylethers. In addition, soft solid lubricants such as molybdenum disulfide (MoS₂) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with
existing spacecraft lubricants, or even unlubricated operation in vacuum. These solid-
and liquid-based tribomaterials show performance in vacuum that differs from that in air,
and even in nitrogen, which contains small partial pressures of oxygen and water. This
issue is especially important for spacecraft hardware, because it is often prohibitive to
test them in a space-like environment, including vacuum, before launch. In this talk,
results will be presented from studies done at The Aerospace Corporation that elucidate
the effects of vacuum and temperature extremes on the tribological performance of
important spacecraft tribomaterials. Emphasis will be on correlating surface chemical
and tribological properties.

This work was funded in part by The Aerospace Corporation’s Sustained
Experimentation and Research for Program Applications program.

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COLL 693

ReaxFF molecular dynamic tribochemistry investigation of a corrugated surface
silica slab

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Geometry and the surface condition greatly affect the tribological properties related to
the lubrication process. In this study, using ReaxFF molecular dynamic simulation, the
mechanisms of friction and tribological characteristics of a corrugated silica surface is
 investigated, while three different surface conditions are applied to the slab: bare silica
surface, hydroxylated surface, and PTFE coated surface. Tribological behavior of
surfaces with different speed and pressure condition is also investigated. The lubrication
results are analyzed using friction coefficients, friction forces, stress, and temperature
distribution of slabs, to elucidate the effects of all different conditions. As a result, we
observed distinctive movements of bumped surface, such as colliding, sliding and
rolling, which result from different pressure and speed during lubrication. In addition, we
checked the effect of various surface conditions influencing the tribochemical properties,
such as friction coefficients.

COLL 694

Do silicon oxide doped DLC (SiOx-DLC) films get help from the environment
during sliding?

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Amorphous hydrogenated carbon (a-C:H) films are widely used as protective solid lubricant coatings in tribo-mechanical applications such as car engines, magnetic storage disks, and biomedical implants. However, these films can exhibit low thermal stability and high residual stresses, and their frictional and wear properties can strongly deteriorate due to changes in the gaseous sliding environment [1]. In the literature, silicon oxide doped diamond-like carbon (SiO_x-DLC) films, also called diamond-like nanocomposite (DLN), exhibit better thermal stability [2] and are less sensitive to the environment [3] than a-C:H films. A convincing model to explain the mechanisms responsible for the improved stability does not yet exist. This work aims to identify the origin of the unique macroscopic tribological properties of DLN films under different environments (ambient air, ultrahigh vacuum, oxygen gas, and hydrogen gas).

Friction experiments were performed with two linear reciprocating pin-on-flat tribometers, one operating in ambient air but allowing gas blowing around the contact, and the other placed inside an ultrahigh vacuum (UHV) chamber allowing gas introduction up to 2 atmospheres and equipped with differential mass spectroscopy [4]. Ambient air tribometry tests using steel counterfaces provide evidence of the dependence of the interfacial shear strength on humidity, and tribotests carried out under UHV conditions indicated that the friction response is mainly controlled by the adhesive interactions between DLN film and the counterface.

In this talk, we will address a key question: does the presence of reactive gases prevent the formation of adhesive junctions by surface passivation, or does it affect the way these junctions are released? A combination of morphological observations and surface analyses are used to help us answer this question.

References :


Challenges and opportunities in the surface characterization of tribological films

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Research in the field of tribochemistry aims to understand the chemical reactions occurring when two bodies are in sliding and or in rolling contact and also to elucidate the mechanism of film formation also in the presence of lubricant additives. Such compounds are intended to reduce wear and control friction, especially when used in the lubrication of mechanical parts under harsh engine oil conditions. At the same time they should be able to reduce energy consumption and be environmentally compatible and sustainable. The synergic combination of experimental and computational resources that is currently applied has the potential to lead to the discovery of new molecules that bring significant innovations in the design of lubricants.

In this presentation, I will review the challenges in obtaining well-defined tribological films with reproducible chemical properties, such that the coefficients of friction and wear can be correlated with changes in the surface properties. Examples will be presented on the effect of sliding time, load, temperature, humidity and oxygen in the tribological performances of films formed in the presence of ionic liquids, zinc dialkylidithiophosphates (ZnDTPs) and phosphorothionates. Special emphasis will be given to the progress achieved by the application of surface-analytical techniques in determining the composition and the structure of the tribological films.

The importance of producing glasses with very well defined chemical and mechanical properties - similar to those compositions identified in the tribological films - will also be discussed, together with the importance of the complementary information obtained by the use of in situ techniques.

Origins of ultra-low friction behaviors of carbon and boric acid surfaces

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The lowest friction coefficient reported in the literature is \( \sim 0.003 \) for highly-hydrogenated diamond-like carbon (DLC) tested in inert environments. DLC films with low hydrogen contents also show a friction coefficient lower than 0.1 in hydrogen gas environments. Graphite is another carbon form that is widely known to exhibit good lubricity in ambient air; it was speculated that the layered crystalline structure is responsible for the good lubricity. But graphite does not work as a lubricant in vacuum
or dry nitrogen conditions. Boric acid is also a lamellar compound with a hexagonal crystal structure similar to graphite. A solid boric acid coating can give a friction coefficient as low as 0.06 for a variety of materials in humid air, but exacerbates friction and wear in an inert environment. Thus, the lamellar structure with weak inter-layer interactions alone cannot explain the excellent lubricity of these materials. In this talk, the chemical origin of super-lubricity of DLC, graphite, and boric acid will be discussed.

**COLL 697**

**Matrix engineering of quantum dot solids**

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Colloidal semiconductor quantum dots (QDs) are attractive building blocks for solar photovoltaics (PV). In this talk, I will provide an overview our ongoing efforts to design lead salt QD thin film absorbers for next-generation PV. Basic requirements for QD absorber layers include efficient light absorption, charge separation, charge transport, and long-term stability. I will first discuss several methods used to make conductive QD films by solution deposition and ligand exchange. Studies of carrier mobility as a function of basic film parameters such as inter-QD spacing, QD size, and QD size distribution have led to a better understanding of charge transport within highly disordered QD films. Efforts to improve carrier mobility by enhancing inter-dot electronic coupling, passivating surface states, and implementing rudimentary doping will be highlighted. Engineering the inter-QD matrix to produce QD/inorganic or QD/organic nanocomposites is introduced as a promising way to optimize coupling, remove surface states, and achieve long-term environmental stability for high-performance, robust QD films. To obtain large photocurrent from QD solar cells, it is critical to increase the minority carrier diffusion length to rival the optical absorption length, possibly by harnessing band-like transport through extended electronic states. The relative roles of superlattice order, energy disorder, and surface states in this regard will be summarized. New results from in situ spectroscopic studies of QD field-effect transistors will be discussed.

**COLL 698**

**Ligand effects in hybrid quantum dot photovoltaics**

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Hybrid quantum dot/polymer solar cells offer the promise of combining the best of quantum dots and organic photovoltaics. To date however, quantum dot/polymer hybrids have lagged in performance behind pure quantum dot solar cells or all-organic PV. By combining transient optical spectroscopy and electronic device measurements we study how different surface ligand treatments can improve open circuit voltage, short
circuit current, and fill factor by influencing charge transfer, transport, and recombination lifetimes in hybrid organic/inorganic solar cells.

COLL 699

Band engineering of ternary lead chalcogenide quantum dots for colloidal quantum dot solar cells

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Recently, quantum dots (QDs) based on low-band-gap metal chalcogenides have been widely explored as photon harvesters in quantum dot solar cells due to their tunable band gap and high absorption coefficient. Colloidal quantum dot (CQD) solar cells made from lead sulfide (PbS) QDs have achieved a power efficiency of ~8%. These types of solar cells consist of a compact/mesoporous TiO₂ layer on a transparent conducting oxide (TCO), followed by a PbS QD layer deposited, and finally a metal which serves as a back contact. In these devices, it is important to control the band gap as well as the band position of the QDs to efficiently inject electrons into TiO₂ and holes into the metal electrode. In this work, studies were performed to control the band gap and tune the relative band positions of ternary lead chalcogenide (PbSeₓS₁₋ₓ) QDs through composition control and surface ligand modification. These effects were studied with UV-Vis absorption and photoelectron spectroscopies. Multilayer CQD solar cells were fabricated to investigate charge mobility between QD layers with different relative band positions. We show that band engineering can be applied to PbSeₓS₁₋ₓ QDs in order to create a favorable band diagram and achieve enhanced photogenerated carrier collection in multilayer CQD devices.

COLL 700

Nanocrystal-inorganic interfaces in composite electrodes

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Over the past few years, we have developed modular methods to integrate colloidal nanocrystals into amorphous inorganic matrices such that a tunable and high density of nanocrystal-glass interfaces are distributed throughout the nanocomposite material. Our approach has been to form chemical bonds linking inorganic clusters to colloidal nanocrystals and subsequently to condense the clusters into a continuous amorphous matrix surrounding, and covalently linked to, the embedded nanocrystals. In ITO-in-NbOₓ nanocomposites the structure of the glassy niobia, probed by Raman spectroscopy, is strongly perturbed near the interface, which we previously correlated
with a five-fold enhancement in optical contrast under electrochemical switching. Now, we use impedance spectroscopy to uncover the improvement charge transport properties responsible for such changes in electrochromic performance. Furthermore, our preliminary results suggest that the chemistry at such interfaces can strongly modify the crystalline phase stability of the nanocrystals. The temperature at which thermally-triggered metastable-to-stable phase transformations occur for nanocrystals in a composite can be tuned by 100 C by changing the nature of the matrix. These observations suggest new strategies for processing of thin film photovoltaic materials from nanocrystals.

**COLL 701**

**Enhanced yield of charge separation in bis-dithiocarbamate-linked zinc porphyrin-CdSe quantum dot donor-acceptor complexes**

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This talk describes the enhancement of the quantum yield of electron transfer (et) from a substituted zinc porphyrin (2-cyano-3-trans-(4-(2-(10,20-bis(2,6-di(n-hexoxy)phenyl)-15-(N,N-diphenylbenzenamine)ethynyl-porphyrinato-zinc(II)-5-yl) ethynyl)phenyl)acrylic acid), abbreviated as “ZnP” to a CdSe quantum dot (QD) upon selective photoexcitation of the ZnP by linking the donor-acceptor pairs with phenyl bis-dithiocarbamate (PBTC) molecules. Quantum yield of et is defined as the fraction of photoexcited ZnP molecules that transfer an electron to a CdSe QD rather than decaying by another radiative or non-radiative pathway. PBTC links the ZnP to the QD by coordinating to Cd$^{2+}$ on the surface of the QD through one of its dithiocarbamate groups and coordinating to the Zn metal center in ZnP with its second dithiocarbamate group. The PBTC linking chemistry increases the fraction of QDs that participate in et with ZnP by a factor of four over that for samples without added PBTC by increasing the average number of ZnP molecules adsorbed per QD. Use of the PBTC linker also increases the observed rate of et by slowing the intersystem crossing of the ZnP ($^{1}\text{ZnP} \rightarrow ^{3}\text{ZnP}$) such that et increasingly occurs through the faster singlet channel ($^{1}\text{ZnP} \rightarrow ^{1}\text{(ZnP}^{+}-\text{QD})$) rather than through the slower triplet channel ($^{3}\text{ZnP} \rightarrow ^{3}\text{(ZnP}^{+}-\text{QD})$).

**COLL 702**

**Silicon nanocrystals with redox active capping ligands**

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Silicon nanocrystals, which are considered as greener alternatives to traditional nanocrystals like CdSe and PbS, offer the benefits of being earth abundant, inexpensive, purportedly less toxic and compatible with silicon electronics. Compared to bulk Si crystal, nanoscale silicon crystals have new properties and functionalities and
are expected to have new and exciting applications in microelectronic, photonic, photovoltaic and nanobiotech industries. A significant rise can be seen in the number of publications on silicon nanocrystals recent years, which witnesses a rising interest in this material. As presented in our research here, the newly designed and synthesized silicon nanocrystals with redox active capping ligands exhibit intriguing electronic properties. This type of materials addresses some fundamental problems such as in what degree the surface determines the property of the nanocrystal as a whole. Moreover, in terms of application, they can also be promising candidates for microelectronic devices. This presentation will focus on the synthesis of the novel silicon nanocrystals capped with ferrocene, fullerene and tetrathiafulvalene based ligands and the characterization of the electronic and optical properties. Several new structures of silicon nanocrystals will be discussed. The potentially interesting redox tunability that these materials offer will also be presented. Initial data have shown that the electronic and optical properties can be affected by the oxidation state of the redox center within the ligands, which can be tuned by potential control.

COLL 703

Manipulating nanocrystal doping, structure, and photocatalytic activity with organic ligands

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Organic ligands (or surfactants) are key in determining colloidal nanocrystal structure and, therefore, function. In addition to their more traditional role as surface passivating agents impacting nanocrystal size and shape, surfactants can also behave as active reagents during the synthesis, hence influencing reaction paths and chemical potential. Herein, we highlight the critical role of surfactants in controlling doping kinetics and granting access to metastable crystalline phases by considering two different photocatalytic oxide systems as examples: TiO₂ and BiVO₄.

In both cases controlling doping, crystalline phase and surface chemistry is essential to manipulate their photocatalytic function. In fact, substitutional anion doping (i.e. N, S and C) in TiO₂ and other binary metal oxides (WO₃, Ta₂O₅) and cation doping (i.e. Sb, Pb) in BiVO₄ have been shown to contribute reducing the band gap and enhancing the absorption in the visible range of these classes of metal oxides.

In the case of binary oxides, we show that it is possible to intentionally position nitrogen in interstitial or substitutional sites depending on the amines used as surfactants during the synthesis. Our UPS/XPS measurements and UV-Vis absorption spectroscopy,
supported by density functional theory calculations, highlight the importance of both nitrogen content and location in determining the defect states position within the oxide band gap and, consequently, the oxide band gap reduction expected in case of hybridization of nitrogen and oxygen 2p orbitals.

In BiVO₄ doping, it is important not only to effectively substitute bismuth with the dopant cations but also to stabilize the more catalytically active monoclinic phase versus the thermodynamically stable tetragonal phase. We demonstrate that the choice of proper reaction conditions and, especially, of surfactants is crucial to this purpose.

Finally, we will briefly discuss preliminary results illustrating the impact of post-synthetic surface treatment on the photoelectrochemical activity of doped TiO₂ and BiVO₄ nanocrystal-based electrodes.

**COLL 704**

**Elucidating the role of polymeric ligands on structure formation and particle interactions in self-assembled nanoparticle array structures**

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The ability to integrate nanoparticle arrays into commercial devices for a range of applications (i.e. quantum dots for light-emitting devices) has been hindered by the generally weak cohesive interactions and the limited processibility of particle solids. Surface-initiated atom transfer radical polymerization offers a novel synthetic route for grafting polymers from particles (known as 'particle brushes') to modulate interparticle interactions. Model systems based on polystyrene-grafted silica nanoparticles were synthesized to systematically evaluate the effect of chain architecture on order formation and mechanical behavior of particle-brush assemblies. A sensitive dependence of the order formation as well as the physical properties of particle-brush solids on the architecture of surface-grafted chains will be demonstrated and interpreted on the basis of a scaling model. Polymer graft modification will be shown to facilitate the fabrication of colloidal superlattice structures by high throughput polymer processing techniques such as spin casting or micromolding. The application of these techniques to the fabrication of photonic materials will be demonstrated.
Hybrid colloidal structures based on plasmonic metal nanoparticles

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Metal nanoparticles in the size range of few to hundred nanometers possess phenomenal physical and chemical properties. It is well known that i.e. chemical inert bulk gold becomes a surprisingly good catalyst when smaller than 10 nm. Strong spatial confinement of surface plasmon polaritons propagating between the metal-dielectric interface have unique optical properties and generate high electromagnetic fields at edges or between particles, leading to applications like SERS (surface enhanced raman spectroscopy). Besides many useful applications metal nanoparticles are of particular interest because of their ease of synthesis and the variety of shapes and surface modifications, which alter the chemical and physical properties. We focus on the synthesis of gold and silver nanoparticles with different shapes because of their absorption in the range of visible light. These nanoparticles can afterwards be modified to produce hybrid core-shell structures with different approaches. Dye molecules and quantum dots can be attached in-situ or by post-treatment into silica or polymer shells to study their optoelectronic properties. Useful effects when emitter and acceptor are
spatially and spectrally overlapping can be quenching or enhancement of the fluorescence or stimulated emission. Besides optical properties of particles in solution we also investigate single particles by a setup that is equipped with a confocal microscope with single molecule sensitivity where the nanoparticles can be identified and manipulated by an atomic force microscope at the same time [1].


COLL 706

Hybrid mesoporous materials by assembly of colloidal particles and pore filling

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We prepared novel hybrid mesoporous materials by assembly of silica colloidal particles or SiO$_2$@Au core-shell particles, followed by pore-filling of the resulting colloidal crystals using surface-initiated polymerization inside the mesopores. We conducted extensive studies of the molecular and ionic transport through these materials as a function of the mesopore size, polymer structure and environmental conditions such as pH and temperature. We demonstrated that pore-filled colloidal crystals constitute a novel type of responsive hybrid materials with potential applications in sensors, separations, drug release and fuel cell membranes. In this talk, we will describe in detail the preparation and transport properties for three examples of these materials: silica colloidal membranes pore-filled with poly(2-(dimethylamino)ethyl methacrylate), colloidal crystals based on SiO$_2$@Au core-shell nanospheres pore-filled with poly(methacrylic acid), and silica colloidal membranes pore-filled with poly(3-sulfopropylmethacrylate). Finally, we will describe the formation of mesoporous membranes via the self-assembly of polymer-modified silica colloidal spheres. The spheres carry polymer brushes grafted on the surface of silica through atom transfer radical polymerization (ATRP) and are held together by non-covalent interactions between the polymer brushes.

COLL 707

Design and response of hybrid conjugated polyelectrolyte-polyoxometalate supramolecular networks

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Simultaneous control of both the optoelectronic properties and morphology of conjugated polyelectrolytes (CPEs) is a critical requirement for their implementation into high performance organic electronics. Physical interactions (e.g. hydrogen bonding, ionic, π-π stacking) between a CPE and an oppositely charged species can be
harnessed to construct hybrid CPE networks with well-defined structural organisation. The challenge, however, is to identify physicochemically compatible organic and inorganic building blocks, which both resist phase separation and introduce the possibility of synergistic functionality to the material.

Here we will demonstrate a novel approach for the preparation of optically-active hybrid supramolecular networks based on the electrostatic co-assembly of cationic CPEs with an anionic lacunary polyoxometalate (POM), $K_8[SiW_{10}O_{36}]$. Using a combination of spectroscopic techniques (UV/Vis absorption, fluorescence, linear dichroism, dynamic light scattering), we observe that the dimensionality of the hybrid network in solution can be tuned from 1D to 2D by changing the molecular weight and steric charge distribution on the CPE. Moreover, atomic force microscopy and scanning electron microscopy studies reveal that the self-assembled hybrid suprastructures generated in solution can be transferred to solid-state thin films. Given the breadth of molecular topologies, surface charge densities, redox and optical properties afforded by both the CPE and POM families, our approach should enable the generation of a variety of well-defined, supramolecular architectures with enhanced functionality.

COLL 708

Magnetic micelles as therapy and diagnostic agents

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The aim of the project is to synthesize iron oxide magnetic nanoparticles (MNPs) in situ within the core of arborescent copolymer micelles consisting of polystyrene-g-poly(2-vinylpyridine) (PS-g-P2VP). These unimolecular micelles appear ideal as templates for the synthesis of inorganic NPs with a pre-determined particle shape and size distribution. Colloidal stability and stealth properties, enabling their in vivo applications, will be provided by a hydrophilic block copolymer through polyion complexation with the P2VP grafts. The potential applicability of these colloidal nanoparticles micelles in inducing cell hyperthermia and as contrast agents for magnetic resonance imaging, as well as their biocompatibility will be evaluated.

The stabilizing block copolymer poly(acrylic acid)-b-poly(2-hydroxyethyl acrylate) (PAA-b-PHEA) was synthesized by atom transfer radical polymerization (ATRP) with good control over molecular weight ($M_n \sim 7, 18$ and $30$ kDa, $D < 1.16$). Particles with a hydrodynamic diameter in the 50-200 nm size range (PdI < 0.18) in buffer (pH 7) can be readily obtained and tuned through modification of the PAA-b-PHEA chain length, which was also used to balance the contribution of steric and hydrophilic stability induced by PHEA versus electrostatic stability provided by PAA. While maintaining the length of one block, decreasing the length of PAA or increasing the length of PHEA increases...
particle stability. These observations were attributed to a reduced particle flocculation, even when complexes with less negative zeta-potentials were formed.

The synthesis of iron oxide MNPs, either by co-precipitation or in situ oxidation/reduction, required particle stability under basic conditions. As compared to the naked arborescent copolymer, the complex particle displayed a good templating potential, yielding stable, water-soluble micelles loaded with iron oxide. Further studies will include improvement of the polymer templating effect and maximization of particle magnetization.

COLL 709

Unique hybrids of silver nanoparticles and tris [3-(trimethoxysilyl) propyl] isocyanurate (TTPI): Controlled fabrication, characterization, and their application in catalysis

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Large scale solution based assembly of nanomaterials with predefined optoelectronic properties is a very challenging task because it requires precisely controlled chemical composition and tight placement of the components. In this regard, quite a few recent reports have shown the potential of self-assembly in designing families of novel materials with preplanned physical and chemical properties.

In this presentation, we will disclose a high yield fabrication strategy to produced self-assembled arrays of silver nanoparticles. The self assembled arrays of silver nanoparticles are produced in organic solvents via reduction of silver nitrate in presence of TTPI/TOA couple. In this process no additional reducing agents is required because combination of TTPI/TOA not only stabilizes the nanoparticles but also act as reducing agent. Using IR and NMR, we will demonstrate that in this case the particles are stabilized via coordination of the nitrogen and carbonyl of the isocyanurate ring of TTPI. One of the very beneficial features of this strategy is that the nanoparticles are stabilized by TTPI, which can undergo hydrolytic condensation polymerization reactions to provide a well defined network which entraps the self assembled nanoparticles. The characterization of self assembled arrays and polymerization of TTPI to produce gel nucleated nanoparticles was carried out using TEM, SEM, UV-vis, IR and NMR techniques. In addition, we will present the preliminary studies of the catalytic activity of self assembled nanoparticles in 4-nitrophenol reduction reaction.

COLL 710

Self-assembly and alignment of organo-soluble functional gold nanorods¹
Compared with isotropic spherical gold nanoparticles, anisotropic gold nanorods (GNRs) are particularly fascinating and challenging due to their unique shape-, size-, and surface-dependent properties. Through their surface functionalization, GNRs can be functionalized as well as be stabilized to have good compatibility for homogeneous dispersion in different media. When doping them in organic medium such as liquid crystal, the GNRs could be further aligned. In addition, some molecules on the surface of GNR could work as molecular “glue” to assemble in specific patterns including end-to-end and side-by-side fashions, which could show the unique collective properties different from those of individual GNRs or bulk materials. In this talk, we will present our recent progress on Self-assembly and alignment of organo-soluble functional gold nanorods.

1Supported by the Air Force Office of Scientific Research (FA9550-09-1-0254)

COLL 711

Self-assembled metallic-dielectric hybrid 2D nano arrays

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We developed a template guided self-assembly approach for integrating metallic and dielectric nanoparticles into metallo-dielectric hybrid materials with defined lattices, which provides new opportunities for the manipulation of light-matter interactions. Arrays comprising nanoparticles of different composition represents an alternative strategy for hybrid materials with new electromagnetic properties that reach beyond those of the individual building blocks. However, the fabrication of this hybrid material is challenging due to difficulties associated with the selective positioning of multiple building blocks at pre-defined lattice We demonstrate that template guided self-assembly strategies provide a viable approach to 2-dimensional hetero-nanoparticle arrays with complex morphology. We create two types of hybrid structures through a template-guided self assembly strategy, which facilitates the anchoring of TiO2 nanoparticles and Au nanoparticle clusters at pre-defined lattice sites. In one geometry individual TiO2 nanoparticles are immobilized on top of a pre-assembled Au nanoparticle cluster; in the other geometry TiO2 nanoparticles and Au nanoparticle clusters are localized in orthogonal lattice sites. The characterization of these materials through elastic and inelastic scattering spectroscopy revealed that the discrete Au nanoparticle cluster - TiO2 nanoparticle structures result in an efficient focusing of the incident light into the metallic nanocluster. In the hetero-nanoparticle arrays the incident
light can excite delocalized surface modes that interact with the plasmonic clusters in the array, which results in a cascaded near-field enhancement. Both investigated structures show a near-field redistribution that leads to an enhancement of electric field intensity not only the in the metal nanoparticle clusters but also in the surrounding ambient medium.

COLL 712

Regulating the intermittency of CdSe/ZnS quantum dots through controlled charge transfer

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Quantum confined nanocrystals have been heavily studied due to their unique properties which can be potentially utilized in light harvesting, light emission or biological applications. However, photoluminescence blinking of quantum dots (QDs), or the on/off switching of their emission under continuous illumination, significantly affects the device performance; thus, controlling the intermittency behavior of QDs and understanding the mechanism behind are critically important. In this presentation I will discuss the effect of external charge traps on the blinking of isolated CdSe/ZnS Qdots. I will show that it is possible to bias the on-time of isolated Qdots by coupling them to specific charge traps, for example to electron acceptors (decrease in on-time) or hole acceptors (increase in on-time). Further control can be achieved by changing the QD's core size as this affects the driving force for charge transfer between QD and both electron and hole traps.

COLL 713

Synthesis of inorganic nanocrystals with systematic shape evolution

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In this talk, I will present our work on the syntheses of Au,1,2 Cu2O,3 Ag2O,4 and PbS5 nanocrystals in aqueous solution with systematic shape evolution. Cubic, octahedral, rhombic dodecahedral, and their intermediate structures have been prepared. The crystal growth is generally done at room or low temperatures and requires only short reaction times. It was found that slight tuning of the reaction rates by adjusting the amounts of reducing agents added in the growth of Au and Cu2O nanocrystals, or by drastically lowering the reaction equilibrium toward product formation in the growth of Ag2O nanocrystals, systematic shape control of particles can be achieved. The polyhedral Au nanocrystals can also serve as cores in the fabrication of Au–Cu2O,6 Au–Pd,7 and Au–Ag8 core–shell heterostructures with systematic shape control. The
successful preparation of these nanocrystals enables the examination of their facet-dependent properties.

References


Coll 714

Mobility of aluminium oxide nanoparticles: Experimental and sensitivity analysis

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The need to develop a deeper understanding of the nature, fate and behavior of nanoparticles in the environment is driven by the increased use of engineered nanoparticles in consumer products. In this study, the mobility of two sizes of aluminium oxide nanoparticles in saturated sand was investigated under different experimental conditions. The filtration of these particles showed significant dependence on several factors such as ionic strength, flow rate, nanoparticle concentration, nanoparticle size, aggregation tendency, solution pH and the method of preparation of the nanoparticles. Diffusion was found to be the predominant mechanism for nanoparticle contact with the sand surface. The ~200nm particles were less mobile likely due to straining whereas the ~80nm particles underwent blocking. In addition, the experimental data was fitted with a transport model in order to further explain the transport mechanisms and apply uncertainty quantification to identify parameters that are important to the mobility of these particles. The two kinetic sites model (two attachment sites and a blocking function) was applied to the experimental results and fitted well. The same model was used to simulate breakthrough curves under different conditions using experimental data and to calculate the 95% confidence bounds over the generated breakthroughs. The sensitivity analysis results showed that slow attachment was the most sensitive parameter for high influent concentrations and the maximum solid phase retention capacity was the most sensitive parameter for low influent concentrations. Results from sensitivity analysis also showed that for particle
size less than \( \sim 1\mu m \), the efficiency due to diffusion showed greater influence on overall single collector contact efficiency. This study indicates important implications regarding aluminium oxide and metal oxide nanoparticle mobility in sand filtration systems, groundwater remediation sites or natural subsurface porous media and that favorable conditions may not be effective for nanoparticle removal.

**COLL 715**

**Eliminating bias-stress effect in PbSe quantum dot field-effect transistors**

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Quantum dot (QD) field-effect transistors (FETs) have received much attention with recent efforts in increasing its field effect mobility >10 cm\(^2\) V\(^{-1}\)s\(^{-1}\) which are now comparable to those of hydrogenated amorphous silicon (a-Si:H) FETs. However, the electrical stability of QD FETs is a critical issue that must be addressed especially if they are to be considered for commercialization. During operation, continuous gate and source-drain biases can influence device performance. In particular, threshold voltage shifts and on-current changes upon prolonged gate bias will disrupt properly functioning FETs. More importantly, it can also overestimate FET performance especially measured mobility. The general reason for this bias instability is typically attributed to charge trapping. Since FETs are layered structures that consist of the semiconductor, gate dielectric, and source-drain electrodes, each layer acts as a critical interface that must be accounted for. The semiconductor, dielectric, and semiconductor/dielectric interface are found to play the most important role in the bias-stress stability.

In this talk, I will demonstrate a universal surface modification that forms air-stable, high mobility, and current transient free lead chalcogenide quantum dot field-effect transistors. I will also address the reason for the variable instability in lead chalcogenide semiconductors because of the variation in the numbers and type of charge (hole or electron) traps that are created in these disordered semiconductors.
We demonstrate the effect of the selective introduction of gold catalytic sites on CdSe@CdSe nanorods on the frontier orbital energies and kinetics of charge transfer processes using waveguide spectroelectrochemistry and photoemission spectroscopy. Reversible electron injection into spin-coated submonolayers of CdSe@CdSe nanorods, Au-CdSe@CdSe rods and welded Au-CdSe@CdSe rods on indium tin oxide (ITO) substrates was observed. The conduction band edge was estimated for each heterostructure by measuring the onset potential for the optical bleaching of the first excitonic peak. The ionization potential (IP) and interface dipole effects of the above hybrid materials were characterized using He(I) and He(II) UV photoemission.
spectroscopy (UPS). Changes in the conduction band, valence band and local vacuum level work function were observed upon tipping of CdSe nanorods with gold. Approximately 50-100 meV conduction band shifts closer to local vacuum level were revealed by spectroelectrochemistry. Potential-modulated attenuated total reflectance (PM-ATR) was utilized to measure the apparent heterogeneous rate constants of reversible electron injection processes. The rate constants for Au-CdSe nanorod hybrid structures were found to be higher than that of the untipped CdSe@CdSe nanorods. The importance of characterizing frontier orbital energies and kinetic parameters of hybrid materials for future development of photoelectrochemical devices is discussed.

COLL 717

Where top-down and bottom-up methods meet: An electrochemical synthesis of colloidal metal and metal oxide nanocrystals using alternating voltages

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Metal and metal oxide nanocrystals (NCs) are important materials for many applications, such as noble metals for heterogeneous catalysis, group IV elements for rechargeable batteries, and transitional metal oxide semiconductors for photovoltaics. Nanocrystals are typically synthesized via top-down or bottom-up methods. However, few syntheses integrate the advantages of both strategies. Here we report such a method, which is simple, generic, and of high atom and energy efficiency. This method, entitled alternating voltage induced electrochemical synthesis (AVIES), has been demonstrated through the production of highly dispersed metal (Au, Pd, Pt, Sn, and Ag) and metal oxide (Ag₂O, ZnO and TiO₂) nanocrystals. The respective nanocrystals are produced when a zero-offset alternating voltage is applied to a pair of identical metal wires, which are inserted into an electrolyte solution containing capping ligands. Interestingly, the nanocrystals are formed on the electrode surfaces and not in the solution. In the case of Au, the obtained nanocrystals are highly crystalline nano-icosahedra of 14 ± 2 nm in diameter, the smallest Au icosahedra synthesized in aqueous solutions via green chemistry. Their catalytic activity has been demonstrated through facilitating the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride. This AVIES approach is an environmentally benign process and can be easily adopted by researchers.

COLL 718

Distinct structural behavior and transport of TiO₂ nano- and nanostructured particles in sand

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Environmental impact of TiO$_2$ particles along with other widely-used nanomaterials as a new class of contaminants has recently emerged. Due to the lack of detailed information and proper understanding of their properties as a result of synthesis (nanoparticles vs nanostructured particles), there is a disagreement in interpreting their behavior and transport in the environment. In this study, we discuss the characteristic retention and breakthrough of commercially available TiO$_2$ particles with unique nanoscale structure, i.e. well-defined nanoparticles (NPs) and nanostructured particles (NSPs), through sand under various reaction environments. NPs such as P-25 (30 nm) were completely different in terms of their physicochemical structure from NSPs, which may be more proper to be considered as micro or bulk TiO$_2$ particles. Such observation undoubtedly evidenced an important finding that encapsulating NPs with stabilizers such as carboxymethyl cellulose, abundant in the environment, and changing their surface chemistry with pH and ionic strength can greatly affect their dispersion in the aqueous phase and mobility through a clean quartz medium, while those strategies were not so effective for NSPs. Therefore, it is apparent that the terms NPs and NSPs should be more strictly differentiated in their use in order to avoid any confusion in assessing their mobility in the environment.

COLL 719

Synthesis of alloyed silicon-germanium nanoparticles

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Group IV nanoparticles have been gaining popularity for their potential uses in a wide variety of applications ranging from biomedical imaging to thermoelectric materials. However, several synthetic challenges still need to be addressed, and while several synthetic procedures have been developed for silicon and germanium separately, there is very little work that has been demonstrated for the production of alloyed silicon-germanium (SiGe) nanoparticles. These alloys are particularly interesting due to the potential for fine tuning of the band gap through size and composition control, as well as improved electrical and thermal transport properties relative to pure group IV materials. This talk will discuss the hurdles unique to group IV nanomaterial synthesis, and will present a solution-based synthesis of alloyed silicon-germanium nanoparticles.

COLL 720

Comparison of optical and electronic properties of PbS quantum dot films made using pre-exchange or in situ exchange of ligands
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Solar cells based on layer-by-layer deposition and ligand exchange of oleic acid capped PbS quantum dots (QDs) with 3-mercaptopropionic acid (MPA) is a very promising research field. While the sequential deposition and ligand exchange approach is unarguably well suited for making optically thick QD layers with good electronic properties there are still aspects of the system that are not thoroughly understood. For example: it has not been demonstrated how the performance of MPA capped PbS QD devices depends on the degree of cross linking of QDs. We have prepared colloidal solutions of PbS QDs using an exchange procedure with 3-mercaptopropionic acid. The colloidally stable quantum dots are soluble in DMSO and thought to be MPA-capped. We have characterized the optical absorption and emission properties of the QD solutions, and are ascertaining the ligand identity using standard analytical chemistry techniques. We are comparing the optical and electrical properties of films made by either deposition of pre-exchanged MPA PbS QDs or the above referenced sequential exchange method.

COLL 721

Multifunctional multidentate copolymer with controlled chain length and functionality to generate nanocrystalline hetero-conjugates

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We investigated a different approach to quantum dot surface modification by using a polydentate capping ligands. In this study we have used ADMET to randomly oligomerize two dienes: One containing azide functionality as an active group capable of clicking with acetylene terminated molecule of interest, and one containing carboxylic acid surface coordinating head groups as a binding diene. Varying the Azide-to-acid diene ratio will allow us to control the relative degree of ligand functionality and nanocrystal surface binding ability. Varying the total dienes-to-Ru catalyst ratio will allow us to control the extent of ADMET, which we will enable us to control overall polymeric ligand size. Using ADMET, we have been able to precisely tune the degree of polymerization from as high as 380 all the way down to only 8 monomer units per polymer. Our synthesized polymeric ligand with as few as 10-20 monomer units is able to wrap around polyethylene glycolated CdSe/CdS quantum dots through the hydrogen bonding interactions between hydroxyl group of surface ligands and carboxylic acid pendants of synthesized polymer. The resulting QD-polymer double layer was clicked onto the acetylene terminated gold nanoparticles to build a hetero-conjugate via formation of triazole ring. TEM images as well as EDS line scans were confirmed presence of such assemblies.
Specific ion effects on the thermodynamics of caffeine partition between organic and aqueous phases

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The Hofmeister series ranks the relative influence of ions on the physical properties of various processes in aqueous solution such as protein solubility, protein folding, enzyme activity, micelle formation, and colloidal assembly. All of these aqueous processes involve formation of interfaces between hydrophobic species and its surrounding aqueous solution. Therefore, the behaviors of ion at the interfaces become important. In this presentation, we investigate the thermodynamics of caffeine partition between organic and aqueous phases in the presence of various salts in the aqueous phase. The partition equilibrium constant, Gibbs free energy, enthalpy, and entropy are evaluated. The mechanisms for how ions affect caffeine partition will be discussed in details.

Adsorption of argon on MFI nanosheets: Experiments and simulations

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Zeolite nanosheets are crystalline microporous structures, where the crystal length is limited in one crystallographic direction. Thus, the zeolite forms a sheet with nanometer length scale in one direction. Zeolite nanosheets have a large surface-area compared to the mass of the sample. They are especially interesting for catalysis, since the active sites in the material will be exposed on the external surface of the zeolite. The reactants and product are to less extent limited by diffusing in channels, cages, and between cages, which is usually orders of magnitude slower than diffusion in fluids.

We have studied the adsorption of argon on MFI-type zeolite nanosheets using classical molecular simulations. Adsorption inside the zeolite crystal, on the external surface of the zeolite nanosheets, as well as capillary condensation taking place between neighboring zeolite nanosheets has to be taken into account. Capillary condensation is studied by varying the distance between the nanosheets. Adsorption isotherms from
experiments are compared isotherms obtained from grand-canonical Monte Carlo simulations. From simulations, the local density profile around the external surface can be calculated, in addition to the surface excess adsorption isotherms for argon.

COLL 724

Spreading of ionic liquids on aqueous surface

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The spreading of surfactant on substrates with higher surface tension is practically important such as in painting and printing. Ionic liquids (ILs) are organic electrolytes that are liquids at room temperature. From the viewpoint of interfacial chemistry, almost all ionic liquids, especially those with long hydrocarbon chains, have amphiphilic structures. Thus, like surfactants, they modify the surface tension of water when they are adsorbed on an air/water interface. In this study, we investigated spreading of three imidazolium-based ILs with different alkyl chain length: 1-buthyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF₆]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF₆]), on a thick aqueous substrate (thickness: 5 mm). Because of the presence of the hydrophobic anion [PF₆]⁻, [BMIM][PF₆] is water insoluble, and [HMIM][PF₆] and [OMIM][PF₆] are water immiscible. The spreading was observed by depositing of a droplet of each IL on the aqueous surface where mica powder was sprinkled.

The spreading advanced in a circle whose radius increased with time as \( A t^{\alpha} \). The exponent \( \alpha \) was \( \sim 0.5 \) and tended to decrease with alkyl chain length. While, the prefactor \( A \) increased with increase in alkyl chain length or with decrease in the surface tension of the IL. As the spreading progressed, the periphery of the spreading area became instable and had an unevenness. The instability increased with time. In the IL with longer alkyl chain, the unevenness was more regular and had a shape of gear. The number of the tooth of the gear tended to decrease with time and increase with increase in alkyl chain length. The spreading instability is explained in mathematical analogy to radial fingering in Hele-Shaw cells¹ by taking spreading kinetics of liquids on thick liquid layers² into consideration.

Exploring colloid-surface interactions and anomalous particle transport behavior in silica nanochannels

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Understanding colloidal transport has become increasingly important, with applications in fields from materials science to biology. However, while many of these disciplines involve nanoscale systems, much remains to be understood about the behavior of colloids under confinement. To this end, we have used resistive-pulse sensing, an electrochemical detection technique, to explore surprising material-dependent size selection in polystyrene and silica nanoparticle transport through silica nanochannels. When two different particle sizes are present in equal concentrations in solution, geometric constraints predict that smaller particles will be detected more frequently than larger ones. We find that while this behavior is indeed observed with silica particles, when the particle material is switched to polystyrene a reverse size selection is exhibited, with larger particles passing through the channel much more frequently, suggesting that surface interactions play a key role in determining transport. To further investigate these unexpected results, we have studied the influence of the following factors on particle entrance and transport: particle material, channel geometry, applied pressure, applied voltage, solution pH, and solution temperature. Determining the role of these parameters will not only enable improved separation techniques and more accurate particle characterization, but will also facilitate a better fundamental understanding of important interfacial behavior under confinement.

Liquid-liquid phase separation of dendrimer aqueous solutions

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Liquid-liquid phase separation (LLPS) is an important phenomenon that has been extensively investigated for proteins and polymers solutions due to its applications in the fields of material and separation science and biotechnology. LLPS of macromolecular solutions can be induced by changing physicochemical properties such as temperature, ionic strength and solvent quality. In this work, we explore the ability of aqueous solutions of dendrimers to undergo LLPS. These are synthetic hyperbranched macromolecules with interesting structural properties that make them very appealing for applications such as host-guest chemistry and self-assembly. To our knowledge, no experimental investigation on LLPS has been reported for dendrimer solutions. In this work we show that aqueous solutions containing fourth generation poly(amide amine) (PAMAM) dendrimers with amine (PAMAM-NH₂) or hydroxyl (PAMAM-OH) functionalized surfaces undergo temperature-induced LLPS in the presence of sodium
sulfate. We experimentally characterize the effect of mixture composition on the LLPS temperature and the composition of the coexisting phases at constant temperature (dendrimer/salt partitioning). In the case of PAMAM-NH$_2$, LLPS is induced by lowering temperature. Interestingly, our results for the PAMAM-OH case revealed that the observed phase transition switches from being induced by lowering temperature to being induced by increasing temperature as the salt concentration increases. This behavior is unique and fundamentally different from that observed for polymers and protein systems. To describe the observed experimental behavior, we developed a model based on steric interactions and salt-induced preferential hydration of dendrimers. Our investigation provides guidance for applications of dendrimers in liquid-liquid partitioning methods relevant to host-guest chemistry and separation science, and the preparation of dendrimer-based materials obtained from the coacervation of these macromolecules.

**COLL 727**

**Simulation of a dye molecule solute in nanoscale silica pores: Position, orientation, and thermodynamic driving forces**

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Liquids confined to nanoscale pores deviate from the dynamical behavior of their bulk counterpart. Understanding the molecular level driving forces for these changes is an important step for creating design principles for mesoporous materials in applications as catalysts, sensors, or separation media. A significant slowing of the reorientation timescales or the appearance of new timescales is widely observed. Reorientation timescales are typically determined using time-dependent fluorescence (TDF). It is likely that fluorescent probes, such as Coumarin 153 (C153), experience a heterogeneous solvation environment inside a pore, however it is unclear how this is manifested in the TDF spectrum. While molecular simulations provide an invaluable tool for determining a molecular level picture of this heterogeneity, long timescales and large free energy barriers within the pore make sampling using classical molecular dynamics a challenge. We have used parallel tempering molecular dynamics to improve the sampling of preferential positions of C153 dissolved in ethanol confined in a hydrophilic silica pore. Using this approach we are able to elucidate the thermodynamic driving forces. In particular, the roles of hydrogen bonding, entropy, solvent layering, and pore surface structure are investigated.

**COLL 728**

**Decontamination of absorbing thin film coatings: Relative importance of extraction dynamics and reaction kinetics**

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The decontamination of materials contaminated with highly toxic chemicals is a challenging problem involving transport and reaction of multiple species in multi-phase systems. Transport-reaction models were developed for liquid phase decontamination of thin film polymeric coatings containing absorbed contaminants. The chemical warfare agent O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate (known as VX) was used with several combinations of aqueous-based decontaminant solutions and polymeric substrates. Two primary mechanisms were considered: a) absorption of the decontaminant active species into the coating and reaction with the absorbed contaminant, and b) extraction of the absorbed contaminant into the adjacent decontaminant solution with subsequent reaction. Liquid phase batch reactor experiments revealed the primary reactions and corresponding kinetics for different decontaminants in the absence of an absorbing coating. Extraction dynamics from a contaminated substrate were also studied as a function of solution composition, ionic strength and pH, which change as the decontamination reaction proceeds. Additional experiments were performed in conjunction with an inverse analysis method to obtain model transport parameters for chemical species in the coatings. The experiments involved contaminating a substrate with a fixed VX exposure, applying a decontaminant, followed by a time-resolved, liquid phase extraction of the absorbing substrate via immersion in deionized water, and measuring the residual contaminant by chromatography. Model parameters were uniquely determined using the Levenberg-Marquardt nonlinear least squares fitting technique to best fit the experimental time evolution of extracted mass. The resulting decontamination model provides an accurate quantification of contaminant concentration profile within material, which is necessary to assess post-decontamination exposure hazards from vapor inhalation and direct dermal contact. The dominant decontamination mechanism for different substrate materials and decontaminant solutions was determined by comparing model predictions with experimental measurements of dermal uptake of VX from decontaminated substrates by a skin simulant material.

COLL 729

Selective binding and surface-enhanced Raman scattering of uranyl nitrate hexahydrate

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The significance of uranium for both power generation and nuclear weapons leads to concern as to who has amassed it and for which application it is being employed. These concerns underlie the field of nuclear forensics, which has conventionally relied heavily on lab-based mass spectrometry (MS) to answer those questions as opposed to more mobile spectroscopic methods. Surface enhanced vibrational spectroscopies, such as
surface-enhanced Raman spectroscopy (SERS), based on plasmonic nanostructures, demonstrate exquisite sensitivity towards the structure of surface-bound species and the ability to measure the vibrational spectrum of a single molecule. Furthermore, cyclic imide dioximes have been shown to be highly selective in binding to uranyl and should also bind other 6+ actinide oxycations. With the addition of a thiol tag these molecules should pre-concentrate actinides at plasmonic surfaces allowing for the use of SERS in actinide detection. This will provide the possibility of a highly sensitive, mobile and rapid detection of actinide species which could be used for nuclear forensics. We demonstrate these principles in a new SERS based detection of uranyl nitrate hexahydrate.