COLL 1

Syntaxin molecules reversibly assemble into clusters beneath secretory granules

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Three SNARE proteins, Syntaxin, SNAP25, and VAMP, are necessary to mediate membrane fusion and allow for exocytosis to occur. In this work, we measured the mobility and interactions of plasma membrane associated SNAREs, Syntaxin and SNAP25, in live PC12 cells. We used Total Internal Reflection Fluorescence (TIRF) microscopy to simultaneously image GFP-labeled, plasma membrane associated SNAREs and a red granule marker, NPY-mCherry. Syntaxin displayed confined dynamics that did not depend on its regulatory H_{abc} domain, a portion of the protein thought to regulate the availability of the SNARE motif. Syntaxin also forms clusters on the plasma membrane that partially co-localize with granules. We fully characterized the granule co-localized Syntaxin clusters and determined the number of molecules per granule by measuring the intensity of single Syx-EGFP molecules. Approximately half of the secretory granules located near the cell surface recruit a Syx cluster and proper recruitment required the H_{abc} domain. On average, each granule-colocalized Syx cluster contains a large number of Syntaxin molecules, many more than are thought to be needed to drive membrane fusion.

COLL 2

New insights into protein-membrane interaction from single-molecule TIRF microscopy

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Membrane-targeting protein domains play central roles in many cellular signaling pathways, but it remains challenging to analyze the molecular interactions that stabilize protein-membrane docking. Here, we demonstrate new applications for total internal reflection fluorescence (TIRF) microscopy with single-particle tracking that provide valuable information about the stoichiometry of protein-membrane interaction. Using engineered proteins containing one to three pleckstrin homology (PH) domains coupled by flexible linkers, we find that protein lateral diffusion constants are inversely proportional to the number of tightly bound phosphatidylinositol-(3,4,5)-trisphosphate (PIP3) lipids. In a separate series of experiments, lateral diffusion is also shown to report on the oligomeric state of engineered proteins containing a soluble interaction domain coupled to a PH domain. Measurements and simulations further indicate that frictional contributions of multiple, coupled but well-separated lipids are additive, analogous to the free-draining limit for isotropic fluids. Overall, these advances provide new insights into protein-membrane interactions and bilayer lipid dynamics.

COLL 3

Measuring shape changes in vesicles on supported membranes by polarized TIRFM

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Polarized total internal reflection fluorescence microscopy is a powerful tool to measure shape changes of vesicles attached to surfaces or supported membranes. Theory that takes into account evanescent field polarization, excitation and emission dipole orientation, and shapes of adherent membranes is developed and applied to follow SNARE-mediated vesicle fusion on supported membranes with millisecond time resolution. Fusion of single vesicles bearing the synaptic fusion protein synaptobrevin2 with supported membranes hosting the presynaptic membrane fusion receptor syntaxin1a/SNAP25 happens ~18 ms after docking. Depending on the lipid compositions of target and vesicle membranes, this fast fusion requires 3 to 8 SNARE complexes. Polarized TIRFM shows that the vesicles undergo a dramatic shape change after the onset of fusion. The fusing vesicles flatten and merge into the planar membrane on average within 8 ms after fusion starts. There is no evidence for an observable (>2 ms lifetime) hemifusion intermediate in these experiments.

COLL 4

Membrane structure and dynamics probed by lipid diffusion

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Examples will be given in this talk to show that the diffusivity of individual lipid molecules, which can be measured by fluorescence correlation spectroscopy (FCS), is a sensitive probe of the local and global structure and dynamics of membranes. For instance, it can be used to reveal peptide-induced domain formation in model membranes. In addition, an example will be presented to illustrate how local diffusions can be used to study functionally relevant conformational motions of membrane proteins.

COLL 5

Cationic lipid vectors for gene delivery and gene silencing: Distinct pathways and interactions with cells

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Cationic liposome (CL) vectors are studied both for gene delivery as CL-DNA complexes and gene silencing as CL-siRNA (short interfering RNA) complexes, and related clinical gene therapy trials are ongoing worldwide. Synchrotron X-ray diffraction has revealed distinct self-assembled structures for CL-Nucleic Acid (CL-NA) complexes, and confocal microscopy has revealed CL–DNA pathways and interactions with cells. Enhancement of transfection and silencing efficiencies of synthetic vectors requires a comprehensive understanding of the nature of the interactions of distinctly structured complexes with cell membranes and events leading to release of active nucleic acids within the cytosol. We will describe experiments, with monovalent and multivalent cationic lipids and novel helper lipids, including cholesterol and cubic phase inducing, which when combined with gene expression and silencing assays, provide insight into DNA and siRNA delivery mechanisms and suggest future approaches for enhancing transfection and silencing efficiencies. Funding provided by NIH.

COLL 6

Detect FAK activations at membrane microdomains by FRET

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Proper subcellular localization of focal adhesion kinase (FAK) is crucial for many cellular processes. It remains, however, unclear how FAK activity upon various physiological stimulations is regulated at subcellular compartments, e.g. lipid rafts. We have developed a fluorescence resonance energy transfer (FRET)-

based FAK biosensor, and targeted it into lipid rafts or non-rafts of plasma membrane by lipid modifications. Upon cell adhesion on extracellular matrix proteins or stimulation by platelet-derived growth factor, the raft-targeting FAK biosensor showed a surprisingly stronger FRET response than that at non-rafts, suggesting that the FAK activation mainly occurs at lipid rafts. Further experiments revealed that the PDGF-induced FAK activation at rafts is mediated by the kinase activity of Src, whereas FAK activation induced by adhesion is independent of, and in fact essential for the Src activation. Therefore, our results suggest that FAK is activated at rafts with distinct activation mechanisms in response to different physiological stimuli.

COLL 7

Characterizing passive transport across biomimetic cell membranes with confocal microscopy

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Developing quantitative relationships between molecular structure and cell membrane permeability requires accurate measurement methods. We have developed a method to measure the membrane permeability of small molecules. Giant unilamellar lipid vesicles (GUVs) are imaged by confocal microscopy as molecules permeate the membrane. These images capture the temporal development of the transmembrane concentration field, providing a rich data set. To facilitate rapid buffer exchange for fast-permeating species, a GUV is immobilized in a microfluidic channel. The concentration of the species of interest can be tracked both inside and outside of the vesicle as the buffer is exchanged. To obtain precise permeability values, these concentration measurements are fit to a finite difference model of membrane transport. This technique is compatible with a synthetic membrane we have developed that mimics the compositional asymmetry of eukaryotic membranes. Such systems will allow for a mapping of the relationships between drug structure, membrane composition, and permeability.

COLL 8

Recent progress in understanding the hydrophobic interaction between surfaces in the nm to adhesive contact distance regime

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The current situation is concerning the existence or otherwise of a “hydrophobic interaction” potential between surfaces (rather than molecules) will be reviewed. The review will cover both old and new SFA and AFM experiments in the all-important short-range regime at surface separations below 2 nm down to contact at D=0. I will also present recent SFA results (by co-workers Steve Donaldson, Ted Lee and Brad Chmelka) on the approach, jumps into contact, adhesion and hemi-fusion of surfactant bilayers that have allowed us to quantitatively assess the separate contributions of van der Waals, double-layer, steric-hydration, bilayer elasticity, and hydrophobic forces at small separations. We propose a model that includes an exponentially attractive hydrophobic term (which acts only when the headgroups spread above their equilibrium head group area) that adequately models both the magnitudes and separations of the energy maximum and adhesive energy minimum at contact of the surfactant chains.

COLL 9

Origin of the long-ranged attraction between surfaces with random charge domains

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Long-ranged attractions across water between two surfaces that are randomly covered with (mobile) positive and negative charge domains have previously been attributed to 'hydrophobic' effects resulting from surfactant coverage of the surface. More recently they have been attributed to break-up of the surfactants to random charge domains and to induced correlation of the charges (positive lining up with negative) as the surfaces approach. We now examine this attribution of charge correlation directly.

COLL 10

Measuring hydrophobic interactions with 3D nanometer resolution

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We investigate forces between two nanoscopic hydrophobic surfaces under pure water. One of the surfaces is a multiwall carbon nanotube AFM tip with a radius of curvature of 8.5 nm, the other a hydrophobic domain in a mixed self-

assembled monolayer. The monolayer has domains consisting of hydrophobic dodecanethiol, surrounded by domains of shorter alkanethiols with hydrophilic end groups. On samples with larger hydrophobic domains (30-80 nm), nanobubbles cover the surface when immersed in water. On samples with smaller domains (10-50 nm), nanobubble formation is greatly diminished, and it is possible to do force measurements that are unaffected by nanobubbles. By using dynamic AFM at a frequency of 1.16 Mhz, which is at least 20 times higher than commonly used in liquid, force-distance profiles are measured with high spatial resolution.On hydrophobic domains we find an attractive hydration force from distances of 5 nm and closer that reaches a maximum of 0.1 nN at a separation of 1.5 nm. Surprisingly, we see a smooth transition to repulsive forces at closer separations. Attractive forces are well-fitted by an exponential decay with 0.6 nm decay length, and we find no evidence for a long-range (>5 nm) attractive force on these samples.

COLL 11

Stability of the wetting films formed on hydrophilic and hydrophobic gold surfaces

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Blake and Kitchener (1972) studied the stability of wetting films of water formed on methylated silica and found that the film formed in a 8.6×10^{-3} M KCl solution ruptured at a thickness of 64 nm. The authored thought that the instability arose from the “hydrophobic forces” in the wetting film. In the present work, we monitored the profiles of the wetting films formed on a gold surface hydrophobized with potassium amyl xanthate (KAX) by recording the Newton rings using a high-speed camera. The temporal profiles were used to determine the excess pressure (p) relative to the bulk water, the pressure due to curvature change (p_{cur}) at the air/water interface, and the disjoining pressure (Π) due to surface forces. It was found that film drainage is induced initially by p_{cur} and subsequently by Π. In the wetting film formed on a hydrophilic gold, p decreases sharply due to the presence of a positive Π, resulting in the formation of an equilibrium film. On the surface of the hydrophobized gold, p increases sharply with decreasing film thickness due to the negative Π in the film. From the values of the z-potentials at the air/water and solid/water interfaces, the contribution from the hydrophobic force to the negative disjoining pressure was determined. We found that the hydrophobic force can be fitted to a single-exponential force law with a decay length (D) of 29 nm. The possibility of explaining the accelerated drainage with the slippage at the solid/liquid interface was also explored by numerical analysis. At assumed values of 20 and 40 nm slip lengths,

D decreased to 26 and 24 nm, respectively, indicating that the long-range hydrophobic force is responsible for the instability of the wetting films formed on the hydrophobic surface.

COLL 12

Water at hydrophobic soft surfaces: Molecular structure, bonding, adsorption and penetration

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Aqueous solutions in contact with hydrophobic fluid media play a central role in a wide variety of physical, chemical and biological processes in our everyday lives. Yet little is known about the molecular properties of this ubiquitous junction. In this talk I will summarize the insights that we have gained in how the structure and bonding of water molecules are altered when the surface of water comes in contact with "soft" surfaces of varying hydrophobicities and organic molecular structures. How the resulting interfacial structuring, which often includes the organic medium, affects the adsorption of charged solutes and the penetration of water into the hydrophobic phase will also be discussed. The hydrophobic systems include organic liquids of different structure and polarity, hydrocarbon and fluorocarbon monolayer films and fluorinated polymers. The studies are a unique combination of experimental spectroscopic measurements using vibrational sum frequency spectroscopy, interfacial tension measurements and molecular dynamics calculations.

COLL 13

Water structure close to ordered and disordered hydrophobic surfaces studied by linear and nonlinear vibrational spectroscopies

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The structure of water in the proximity of different hydrophobized surfaces has been investigated using Vibrational Sum Frequency Spectroscopy (VSFS) and Total Internal Reflection Raman spectroscopy in an effort to relate molecular structure to macroscopic surface properties (i.e. contact angle). Two different dielectric surfaces were hydrophobized using silanes and Langmuir-Blodgett deposited fatty acids. Variation in the preparation procedure resulted in surfaces displaying clear differences in both the recorded spectra and the receding contact angles. The water structure and in particular the intensity of the "free OH" vibration (water molecules having a non-hydrogen bonded OH group oriented

towards the hydrophobic surface), was found to be correlated to the degree of order of the hydrophobic monolayer and to the contact angle hysteresis. The sensitivity of VSFS to detect “nano-bubbles” on hydrophobic surfaces will also be discussed.

COLL 14

Hindered rotation of water near C_{60}

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Cross polarization (CP) nuclear magnetic resonance (NMR) experiments show that water within about 1 nm of C_{60} molecules is anisotropic and undergoes rotational motion that is greatly hindered compared to motion in bulk. The experimental observation of Hatman-Hahn CP contact shows that the motion of water is slow enough for intermolecular ^{1}H (water) –^{13}C (C_{60}) dipolar coupling to occur, suggesting that the time-scale of rotational (tumbling) motion of the water adjacent to the C_{60} is slower than the microsecond range. This is much slower than the picosecond range previously observed for bulk water. The dipolar coupling decreases with temperature in the range 3–22°C. This work provides molecular-scale evidence that a small hydrophobic particle can order surrounding liquid water molecules.

COLL 15

Different pathways of nanoparticles entering into cells

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Nanoparticles are widely used as drug delivery vehicles and biosensing agents. In this study, we investigated how different nanoparticles enter into cells using a combined optical spectroscopic study. Fluorescence microscopy was applied to image how different nanoparticles enter into live cells, with and without various endocytotic pathways blocked. Sum frequency generation (SFG) vibrational spectroscopy was applied to investigate molecular interactions between various nanoparticles and model cell membranes. Such interactions can also be measured using vesicle dye leakage experiment. Results obtained from live cell studies are well correlated with those from the model cell membrane studies, elucidating various pathways for different nanoparticles to enter into cells.

COLL 16

Nanomaterial based long range optical ruler for monitoring nanomaterial biological cell interaction

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Optical-based distance measurements are essential for tracking bio-molecular conformational changes, drug discovery and it have been used in a wide range of applications in analytical biochemistry. Last few years we are developing gold nanomaterial based long range optical ruler for probing bio-molecular interaction with nanoparticle and to detect pathogens from environmental samples. In this talk we will discuss our recent report on the design long range optical ruler using nanomaterials surface energy transfer and surface enhanced Raman spectroscopy. We will also discuss how one can use nanomaterial base long range optical ruler for probing nanomaterial interaction with HaCaT and different cancer cell linesa.

COLL 17

Distribution of engineered nanomaterials between model biological membranes and water

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In this presentation, we quantify the pseudo-equilibrium distribution of selected well-characterized engineered nanomaterials (ENMs) between lipid bilayers (LBs), used as model biological membranes, and water. We examine the effects of physicochemical properties of ENMs including size, surface functionalities, and core composition as well as aqueous chemistry. Preliminary data indicate that fullerol aggregates ($C_{60}(ONa)_x(OH)_y$, x + y = 24) reached pseudo-equilibrium faster in 2 h than C_{60} aggregates (nC_{60}) (> 9 h). The LB-water distribution (LBWD) of nC_{60} and fullerol can be described by isotherm-like behaviors. While both nC_{60} and fullerol exhibit pH-dependent LBWD behaviors with accumulation in LBs increasing systematically as pH decreases from 8.6 to 3, the LBWD coefficients of nC_{60} is up to 1 order of magnitude larger than those of fullerol. This pH-dependency parallels the decrease in the electrostatic repulsion between LBs and fullerene aggregates, as the zeta potentials of both increased (i.e., became less negative) as pH decreased. Comparisons with existing bioaccumulation studies that used aquatic organisms suggest that LBWD is promising in assessing the bioaccumulation potentials of ENMs. Ongoing research is focused on the size dependency in the LBWD of gold nanoparticles (nAu) with well-defined sizes from 5 to 100 nm. Preliminary results indicate that 20 nm nAu shows the highest accumulation to LBs.

COLL 18

Influence of solvation and interparticle interactions on the aggregation behavior of nanoparticles in membranes

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Recently, the behavior of nanoparticles in cell membranes has received much attention due to potential biological applications. Due to difficulties in characterizing nanoparticle behavior in this complex environment researchers have looked to strengthen experimental data with computational modeling. Here we study the unusual aggregation behavior of simulated C_{540} particles in DOPC membranes. Through molecular dynamics simulations we show that the nanoparticle-solvent interaction strength plays a critical role in determining the aggregation behavior of nanoparticles confined to a two-dimensional environment.

COLL 19

Real-time characterization of nanoparticle interactions with planar surfaces, cells and biofilms

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There is a growing need for new technologies to quantitatively measure small particle interactions with different types of materials in real-time. One technique in particular, Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D), fulfills the need for monitoring real-time dynamic adsorption and desorption phenomena. Capable of operating in liquid environments, QCM-D provides a powerful approach to analyze the *in situ* thickness, structural, and viscoelastic properties of both nanoparticle buildup at interfaces but also structural changes the nanoparticles themselves may impart to cells or other materials. This presentation will focus on the application of the QCM-D technology to monitoring

nanoparticle - surface interactions. The types of particles that will be covered include quantum dots, metallic and oxide nanoparticles and the surfaces investigated include planar metallic and oxide surfaces, functionalized surfaces, cell surfaces, and biofilms.

COLL 20

Toxic gold: Membrane destabilization due to size of gold nanoparticles measured by a quartz crystal microbalance with dissipation (qcm-d)

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The increase of commercialized products containing nanoparticles has raised concerns about the impact these particles will have on humans and the environment. The aquatic environment may be particularly susceptible to effects of nanoparticles; however, the impact is unknown since full toxicity tests have not been conducted. It is important to understand the mechanism by which nanoparticles less than 20nm enter aquatic cells. The collected data will be used to determine the degree of membrane destabilization and create toxicity guidelines for nanoparticles released in the environment. Gold, an accepted non-toxic material, was used to demonstrate that there is a size range threshold where nanoparticles smaller than 20nm cause toxicity even if the material is nontoxic. Nanoparticles in the range from 2nm-80nm were used to demonstrate the effects. Results show that nanoparticles less than 20nm cause a loss of mass to an Egg Pc lipid bilayer. The change in mass is determined by frequency measurements using a Quartz Crystal Microbalance with Dissipation Monitoring Technology (QCM-D). The mechanism causing the mass reduction of the lipid membrane plays a role in understanding the onset of toxicity as the size of the particles are reduced. This study presents ground breaking evidence that once a particle is translated to a small enough size, it is the size of the particle that causes membrane destabilization. This allows us to address the potential environmental dangers of releasing nanoparticles into aquatic life.

COLL 21

Influence of size, surface properties, and geometry of silica and gold nanoparticles on cellular uptake and toxicity

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The influence of size and surface functionality of silica nanoparticles (SNPs) of 50 and 200 nm in diameter on their interaction with murine macrophages was studied. Confocal microscopy revealed fast kinetics of accumulation and differential intracellular localization of plain, amine- or carboxyl-terminated SNPs in RAW264.7 macrophages. Toxicological effects of SNPs depended on particle size and surface functional groups. In addition, three types of amine-terminated silica nanomaterials were prepared and characterized via the modified Stober method; namely spheres, worms, and cylinders. The findings of the study so far suggest that geometry does not play a dominant role in toxicity and uptake of the SNPs in these cell lines. Gold nanorods (GNR) were surface functionalized with poly (ethylene glycol) terminating in either a methoxy group or the RGDfK angiogenic targeting peptide. A significant increase in GNR binding and uptake with targeted versus non-targeted GNRs in both cell types was observed.

COLL 22

Fluorescence detection of nanoparticle exocytosis

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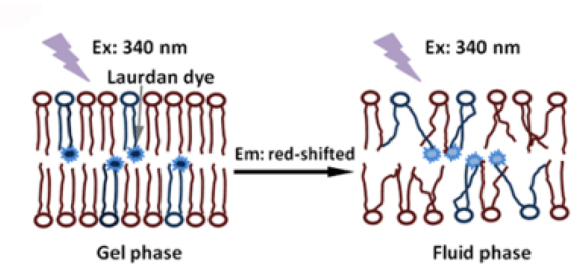
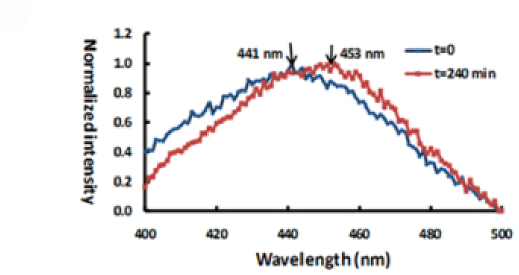
In view of the rapid development of nanotechnology and its vast biological and environmental applications and implications, it is imperative to obtain a database regarding the behaviors of nanomaterials in living systems, especially on the cellular level. This paper examines the exocytosis of nanoparticles, an important but rarely documented aspect of cell responses to engineered nanomaterials. Specifically, HT-29 mammalian cells were labeled with a lipophilic Laurdan dye, and the membrane fluidity in the presence of gold nanoparticles was evaluated by the generalized polarization (GP) values derived from the fluorescence spectra of the dye.





The concentration of excreted gold nanoparticles increased with increasing extracellular calcium, directly demonstrating exocytosis of nanoparticles and corroborating the inference made from the GP values of the Laurdan dye. This study provides additional information for understanding the fate of nanomaterials in biological systems.

COLL 23

Nanoparticle - membrane interactions

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Large nanoparticles of size 20 nm and above are usually considered to be taken up by cells by the mechanism of endocytosis. For smaller nanoparticles, a clear uptake mechanism has not been proposed. We suggest that the mechanism of cell uptake of the smaller nanoparticles and also the mechanism of nanoparticle induced cell disruption to be consequences of purely physical interactions between the nanoparticles and the cell membrane. We consider various modes by which the nanoparticle may interact with a lipid bilayer membrane and the mechanisms by which particle uptake or lipid membrane disruption can occur. Briefly, the adsorption of nanoparticles on the lipid bilayer surface may cause membrane thinning and lipid chain stretching to occur in order to maintain the molecular space filling requirement of the lipid bilayer. Depending on the nanoparticle dosage (nanoparticle to lipid ratio), the unfavorable free energy of membrane thinning and lipid chain stretching may reach a critical value equaling the unfavorable energy of stable pore formation or membrane lysis. At this critical nanoparticle dosage, the structural integrity of the membrane is compromised.

Under alternate conditions, the surface adsorption of the nanoparticle may lead to solubilization of the nanoparticle inside the hydrophobic domain of the membrane. In this case, the membrane structure is not destabilized but a transport of the nanoparticle across the membrane and uptake into the cell becomes possible. We investigate these phenomena in terms of the free energy of nanoparticle-membrane interactions for different sizes and surface polarities of spherical nanoparticles.

COLL 24

Hybrid cells for simultaneously harvesting multiple types of energy

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Our living environment has an abundance of energies in the forms of light, thermal, mechanical (such as vibration, sonic wave, wind and hydraulic), magnetic, chemical and biological. Harvesting these types of energies is of critical importance for long-term energy needs and sustainable development of the world. Over the years, rationally designed materials and technologies have been developed for converting solar and mechanical energies into electricity. Photovoltaic relies on approaches such as inorganic pn junctions, organic thin films, and organic-inorganic heterojunctions. Mechanical energy generators have been designed based on principles of electromagnetic induction and piezoelectric effect. Innovative approaches have to be developed for conjunctional harvesting of multiple types of energies using an integrated structure/material so that the energy resources can be effectively and complimentarily utilized whenever and wherever one or all of them are available. We report a hybrid cell that is designed for simultaneously harvesting solar and mechanical [1,2], and chemical and mechanical [3] energies using nanotechnology. The two energy harvesting approaches can work simultaneously or individually, and they can be integrated in parallel and serial for raising the output current and voltage, respectively. Our study demonstrates an innovative approach for developing integrated technologies for effectively scavenging available energies in our environment around the clock. [1] C. Xu, X.D. Wang and Z.L. Wang, “Nanowire structured hybrid cell for concurrently scavenging solar and mechanical energies”, JACS, *131* (2009) 5866–5872. [2] M.B. Lee^{+},, R.S. Yang^{+},, C. Li, and Z.L. Wang “Nanowire-quantum dot hybridized cell for harvesting sound and solar energies”, J. Phys. Chem. Letts., 1 (2010) 2929–2935. [3] B.J. Hansen, Y. Liu, R.S. Yang and Z.L. Wang “Hybrid Nanogenerator for Concurrently Harvesting Biomechanical and Biochemical Energy”, ACS Nano, 4 (2010) 3647-3652.

COLL 25

Just by squeezing! (Starting with) Hydrogen peroxide production by mechanically treated polymers

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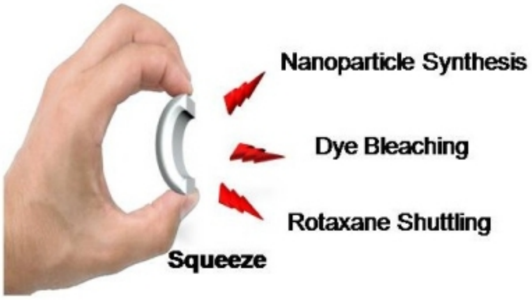
Mechanical stress on certain type of materials can lead in production of chemical energy. Despite the versatile literature on mechanically treated substances dating back to 1950s[1], there is only a limited understanding of the underlying molecular-scale processes[2]. Moreover, nearly all of these systems require permanent macroscopic damage of the material. Here, we present a few examples of many possible chemical reactions – nanoparticle synthesis, dye bleaching and a rotaxane switching[3] can be driven by macroscopically *non-damaging* mechanical compression of flexible polymers; all starting with production of aqueous *hydrogen peroxide*.



The method shown is more general than the existing processes for hydrogen peroxide production using special chemicals and/or electrochemical procedures. It is environment friendly since the polymers can be reused for many cycles without significant loss of efficiency. At the same time, the fact that polymers under stress may produce harmful radicals raises many concerns such as for the utilization of polymer-based implants. Literature and Notes: [1] Grunberg, L., Wright K. H. R., *Nature* **1953**, *171*, 890-890. [2] Konôpka, M. et al. *J. Phys. Chem. C*, **2009**, *113*, 8878-8887. [3] We acknowledge Dr. Sanjeev K. Dey and Prof. J. Fraser Stoddart for generous gift of the bistable rotaxane. This work was supported by the US Department of Energy, Office of Basic Energy Sciences as part of the Non-Equilibrium Energy Research Center (NERC), an Energy Frontier Research Center.

COLL 26

Large scale energy storage: From nanomaterials to large systems

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This talk aims to discuss important cross-cutting, fundamental materials science and materials chemistry challenges that are applicable to a range of technologies encountered in electrochemical storage. This talk will attempt to highlight the critical materials problems using specific examples and results from recent efforts to reduce the cost and improve the performance of electrochemical energy storage devices. Specifically, this talk discusses 1) the characterization and understanding of the complex solution chemistry and redox reactions in concentrated, aggressive electrolyte solutions, 2) approaches to develop new battery designs and new chemistry combinations to reduce the cost, and 3) limitations and challenges of the electrode materials, nanoporous materials and ion selective membranes. In addition, the paper discusses the prospect of emergent technologies with ultralow costs on new energy storage materials and mechanisms.

COLL 27

Slurry-based processing of high-performance CZTSSe photovoltaic absorber layers

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Kesterite $Cu_2ZnSnS_{4-y}Se_y$ (CZTSSe) materials are considered promising for application as thin-film photovoltaic (PV) absorber layers because of appropriate band gap (ranging from 1.0-1.5 eV, as a function of y) and low-cost, readily-available constituents. This talk will focus on a simple particle-based approach for solution processing device quality CZTSSe films. Deposition involves three steps: 1) preparation of the hydrazine-based CZTSSe precursor slurry, 2) liquid-processing (e.g., spin coating or doctor blading) of CZTSSe precursor films on an appropriate substrate, and 3) heat treating to yield the desired CZTSSe layer. High quality films with variable sulfur to selenium ratio (y) are deposited using this approach. PV devices based on a glass/Mo/CZTSSe/CdS/i-ZnO/ITO structure and employing the slurry-processed CZTSSe layer with $y > 2$ (i.e., Se rich) have yielded independently-certified power conversion efficiencies of >9.5% (AM 1.5 illumination), a record for the kesterite family of materials. Recent results using this approach will be discussed.

COLL 28

Synthesis and characterization of Si nanoparticles prepared from reactive Zintl phases for energy applications

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Silicon Nanoparticles are of interests for a variety of applications, from thermoelectrics to photovoltaics. This research group has been exploring various synthetic routes to prepare organically capped Si nanoparticles from reactive Zintl phases such as NaSi. Doping NaSi with various main group and transition elements provides more complex nanoparticles. Synthesis and characterization of the NaSi starting material will be presented along with the synthesis and characterization of the resulting nanoparticles.

COLL 29

Lifting physisorbed colloidal particles from solid surfaces

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This paper describes “rinsing flows” wherein a jet of one fluid ablates a layer of a second, miscible liquid that coats a solid substrate. This process is common to everyday experience and to many industrial processes, particularly cleaning operations. This flow arrangement is accompanied by a classic, “hydraulic jump” phenomenon but the stratification of two liquids, with differing rheologies, leads to qualitatively new results. Of particular interest to one of the applications of this process (the cleaning of colloidal particles from solid, planar substrates) is the case when the liquid coating the substrate (the one being rinsed off) possesses a large elongational viscosity. Data are offered that demonstrate that fluids with large, strain thickening extensional viscosities very effectively “pluck” adsorbed colloidal particles from planar surfaces.

COLL 30

Shear banding and flow-concentration coupling in colloidal glasses

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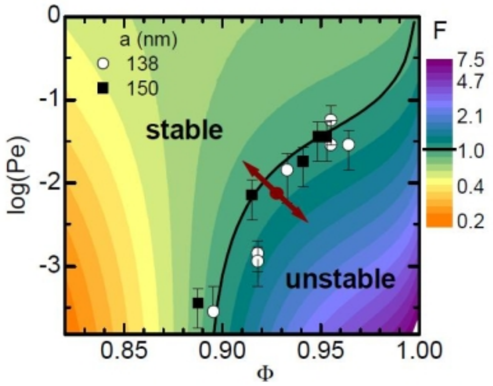
We report experiments on hard sphere colloidal glasses that reveal a type of shear banding hitherto unobserved in soft glasses and present a theory that relates this to an instability arising from shear-concentration coupling. Below a characteristic shear rate we observe increasingly non-linear velocity profiles and strongly localized flows, which we attribute to small concentration gradients arising in the unstable flow regime. The theory quantitatively accounts for the observed phenomenology.



COLL 31

Statistical mechanical theory of the microstructure and rheology of concentrated colloidal dispersions

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In colloidal dispersions, coupling of flow to the microstructure alters the macroscopic rheology. The objective of this work is to predict nonequilibrium microstructure and rheology of sheared hard-sphere colloidal suspensions as a function of ratio of shear to thermal force and the solid fraction. This problem is analyzed by conditionally averaging probability distribution function conservation equation (Smoluchowski equation) for two particles, resulting in an integro-differential conservation equation that is solved using an iterative method. Comparison between the theory predictions and simulation results by Stokesian Dynamics shows this theory accurately predicts the major features of microstructure far from equilibrium (shear-dominated conditions) and concentrated dispersions, which differentiates it from the previous theoretical works in the field. The rheological quantities of effective viscosity and first and second normal stress differences are calculated based on the computed microstructure and compared with Stokesian Dynamics simulation results and experiments, with remarkably good agreement.

COLL 32

Synthesis and rheology of pH-responsive polymer colloids with shape anisotropy

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Rules for equilibrium and non-equilibrium phase behavior of physically and chemically anisotropic particles are not well understood. Experimental demonstration of simulation predictions of novel phase diagrams for particles interacting with anisotropic pair potentials goes slowly due to the difficulty in making anisotropic particles at large scale. Here a seeded emulsion polymerization method is used to produce large quantities of shape anisotropic, amphoteric-particles in 1μm size range. The method used is thought to concentrate cationic groups at one side of the particles. By coating the particles with a stabilizer, weak attractions are introduced by varying pH and ionic strength. Here we investigate the state diagram of these systems and the rheology of concentrated suspensions. The amphoteric particles show a pH of least stability and gels in this region had anomalously large elastic moduli. These results are interpreted in terms of the potential that the particles interact with anisotropic pair potentials.

COLL 33

Dynamics, microstructure, and rheology of polymer-bridged colloidal gels

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We investigate the relationship between the dynamics, rheology and microstructure of polymer-bridged gels of charge-stabilized silica colloids and oppositely charged polyethylimine polymer. The rheology of these gels displays a reentrant behavior upon changing the polymer concentration (C_p). Concurrently, the dynamics and microstructure are probed using quantitative confocal microscopy. At low C_p, a biphasic mixture, consisting of mobile particles coexisting with a set of dynamically arrested particles is encountered. We segregate the particles based on their mobility and identify three consitutent populations: (i) freely diffusing mobile particles, (ii) free particles with restricted mobility, and (iii) completely arrested particles. The arrested population is isolated for quantitative structural analyses. A strong correlation between the stiffness of the gel, heterogeneity of particle dynamics and the volume fraction of the arrested phase is observed. Over the range of concentrations investigated, the reentrant rheology is accompanied by subtle changes in the microstructure of the arrested phase. The origins of this behavior and the implications on the rheology of colloid/polymer mixtures are discussed.

COLL 34

Effect of thixotropic fluid composition and rheological properties on suspension of magnetite particles in a magnetic field

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Control of magnetic fluid stability is important to the application of Ferro fluids in magnetic seals and image contrasting and tumor treatment in medicine. The authors have investigated the stability of magnetite dispersions in varying magnetic field strengths and concentrations of the thixotropic additives xanthan gum and bentonite clay. Optical microscopy in a magnetic field, dynamic viscosity, and elastic modulus recovery as a function of time following sample pre-shearing were used to assess particle stability. Optical microscopy of magnetite dispersions in the additives showed that the particle length to diameter ratio (L/D) in a magnetic field approached a value of 1 with increasing concentrations of the thixotropic materials. Dynamic viscosity data reveal that a plot of magnetite L/D versus the consistency index K was linear and independent of the additive type. Dynamic recovery experiments of the fluid elastic modulus after pre-shearing showed that elastic modulus regain for the bentonite clay was time dependent and much greater than for the xanthan gum, resulting in greater magnetite stability in the bentonite.

COLL 35

Micro-optical sensors and microfluidic and imaging devices for cancer biosignatures

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Engineering methods for microscale devices are being increasingly applied to advantage in fundamental and applied cancer research. We developed technologies for measuring physiological responses, genomics, transcriptomics (mRNA), protein function, and cytostructure at the few- and single-cell level. To accomplish these goals we adapted processes from the semiconductor industry to produce microfluidic devices, known as “labs on chips”, for physiological measurements on individual cells or on a few, interacting cells. We synthesized fluorescent optical sensors and specific reporters for analytes and biomolecules,

either within the living cell or in its surrounding microenvironment. After physiological measurements, we harvested the cells to analyze their genome and transcriptome. In parallel, we developed a capillary-based method for single-cell 3D computed tomographic (CT) imaging of cell structure by absorption and cell function by fluorescent reporters of protein expression level and subcellular location. We derive integrated biosignatures sensitive to cancer progression stage from this set of measurements, for eventual application to early cancer diagnosis.

COLL 36

Characterization of circulating tumor cell dry mass, pathlength distribution, and cellular organization using differential interference contrast based quantitative phase imaging

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Circulating tumor cell (CTC) enumeration and characterization has the potential of providing insight into the aggressiveness of cancer growth and metastasis in cancer patients and may assist in therapeutic decisions regarding diagnosis, staging, and treatment. Owing to their ultra-low concentration in blood and the difficulty of their detection, currently little quantitative information is known about the physical properties of CTCs. In this study we utilize quantitative phase microscopy based on the transport of intensity equation analysis of differential interference contrast imaging to characterize physical properties of CTCs identified in cancer patients through fluorescence staining technique called CTC-ID. Phase recovery enables the quantification of CTC dry mass, pathlength distribution, and cellular organization. We demonstrate the potential of these physical properties to serve as label-free biomarkers of CTCs.

COLL 37

Toward theranostics via magnetic nanostructures (MNS)

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The emerging cross-disciplinary “nano-bio paradigm” promises considerable excitement for scientists and engineers, with tangible prospects for revolutionary applications for technologists as well as clinical practitioners. Our research efforts in this area are geared towards designing complex architecture of magnetic nanostructures (MNS) as well as using them as building blocks for device systems for sensing, diagnostics and therapeutics (theranostics). Embedded in

this broad scheme are several approaches based on magnetic nanostructures (MNS) as MRI T2 contrast enhancing agent and for combined T2-T1 imaging modalities, carriers for site- and target-specific drug delivery and therapeutics, among others. The presentation will outline emerging understanding of the role of composition, size and shape-dependent properties and characteristics of MNS. The presentation focus will be on MR relaxivities and thermal activation as it relates to MNS variables, with examples to specific targeting for model cancer cell lines, medulloblastoma pediatric tumor cells and proteins associated with Alzheimer's disease.

COLL 38

Amyloidogenesis detected by chiral sum frequency generation spectroscopy

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A molecular understanding of amyloidogenesis is important to develop small-molecule drugs for its inhibition and elucidate the pathogenic origin of amyloid diseases, such as Parkinson's and Alzheimer's diseases. We applied chiral sum frequency generation (SFG) spectroscopy to investigate the kinetics of the early stage of the aggregation of human amyloid islet polypeptide (hIAPP). Using the chiral SFG vibrational signatures of protein secondary structures that we recently identified, we observed in real time the misfolding of hIAPP from random-coils to alpha-helices and then beta-sheets upon interaction with the lipid/water interface. We further demonstrated that a chiral vibrational signal at 1620 cm^{-1}, a highly characteristic amide I frequency for parallel beta-sheets, can be detected from the aggregates formed by not only hIAPP, but also alpha-synuclein and amyloid beta-peptide, which are implicated in Parkinson's and Alzheimer's diseases, respectively. The results suggest the potential of chiral SFG for *in vivo* and *in vitro* amyloid detection.

COLL 39

Targeted gold nanobeacons and photoacoustic imaging of angiogenesis may augment ultrasound diagnosis and management of atherosclerosis

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While ultrasound (US) following intramural injection of microbubbles can detect increased vasa vasorum, it cannot recognize angiogenesis specifically. Photoacoustic tomography (PAT), a new ultrasound enhancing technology, permits visualizing microvasculature anatomy and oxygenation. The objective of this study was to develop integrin-targeted gold nanobeacons to specifically detect and differentiate angiogenesis from mature microvasculature. Lipid-encapsulated gold nanobeacons (GNB) (~140 nm, PDI 0.06) were synthesized by incorporating tiny gold spherical nanoparticles (2-4 nm) and homed using a lipid-conjugated peptidomimetic avb3-intergrin antagonist (250/GNB). The concept of angiogenesis imaging with PAT was studied in a Matrigel plug mouse model using PAT detection system. In Matrigel-implanted mice PAT images were acquired at baseline and hourly thereafter. No significant change in enhanced pixel number was measured between baseline and later images for mice given saline and nontargeted GNB. However, the appearance of angiogenic sprouts was grossly apparent between baseline and later images in mice given targeted GNB.

COLL 40

Thrombus-specific “NanoQ” copper nanocolloids for MR molecular imaging of ruptured atherosclerotic plaque

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Detection of thrombus within fissures of vulnerable atherosclerotic plaques requires a sensitive molecular imaging contrast agent. However, nephrogenic systemic fibrosis has recently raised concern over the use of currently approved gadolinium based contrast agents in patients with impaired renal/kidney function and created a high translational barrier for new agents. Considering this, we explore for the first time copper (Cu) as a paramagnetic nanoparticle agent for molecular imaging. “Soft” type nanocolloids of copper oleate (NanoQ) were designed and synthesized as vascularly-constrained (D_{av}=217 nm, z=-13mV) nanoparticles and characterized for MR. Organically soluble copper (II) oleate was suspended in polysorbate and encapsulated by phospholipid mixture to incorporate nominally 100,000 Cu/particle. Acellular fibrin clots were targeted with biotinylated NanoQ or control nanocolloids to the fibrin clots with avidin-biotin interactions and fibrin-specific antibodies (NIB5F3). MR (3T) imaging of NanoQ showed clear contrast enhancement, while control clots (non-targeted and untreated) had no (or negligible) contrast change.

COLL 41

Towards an early Alzheimer's diagnostic using magnetic nanostructures for MR imaging of synaptotoxic amyloid-beta oligomers (ADDLs)

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No clinically relevant diagnostic currently exists for early-stage Alzheimer's disease (AD). Since diagnosis of AD is obtained only through post-mortem autopsy, the development of an early diagnostic is greatly needed. Increasing evidence supports the role of oligomeric Amyloid-Beta Derived Diffusible Ligands (ADDLs) as the potent neurotoxic species in AD, which bind to synapses, prevent LTP, decrease dendritic spine density, elevate reactive oxygen species, and lead to neuron death. ADDL-specific monoclonal antibodies produced in the Klein Lab, including NU4, bind A-Beta oligomers, preventing their binding to neurons and the subsequent toxic response. In developing a highly sensitive AD diagnostic, we propose the use of biocompatible superparamagnetic Fe3O4 nanostructure conjugates with NU4 antibody for use with clinical magnetic resonance imaging (MRI). These NU4-MNS conjugates provide high T2-relaxivity and ADDL specificity. In vitro fluorescence microscopy experiments have demonstrated that NU4-MNS target synthetic ADDLs as well as ADDLs in human plaques. NU4-MNS treated human AD brain slices produced significant T2-weighted MR contrast compared to control, showing promise towards developing an early-stage AD diagnostic.

COLL 42

Self-assembly of the oligo(ethylene glycol) linked dinitrophenyl terminated disulfide on gold investigated by atomic force microscopy

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DNP-terminated SAMs have been fully used to activate mast cells, thus this presentation deals with the packing of DNP thiols within self-assembled monolayers (SAMs). Oligo(ethylene glycol) linked dinitrophenyl terminated disulfide (DNP) on gold are characterized by high-resolution atomic force microscopy (AFM) imaging and nanografting. Local domain structures, film thickness and surface roughness of these SAMs are highly sensitive to solvents used. The DNP SAM forming in DMF and 2-butanol mixture solvent exhibits domains with irregular shapes and an average film thickness of 3.9 ± 0.4 nm. In

contrast, in DMF and ethanol, a binary layer of DNP films is observed. Mast cell behavior on DNP SAMs will also be discussed.

COLL 43

Block copolymer coated magnetic nanoparticles as hybrid systems for combined imaging and therapy of brain diseases

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Magnetic nanoparticles are currently widely investigated and used in life sciences as contrast agents for biomedical imaging applications as well as heating sources for hyperthermia. However, their lack of stability in *in vivo* conditions, their potential toxicity due to ion leakage and their poor stealthiness and targeting abilities must be improved through chemical modifications of their surface. Polymers and copolymers have been widely used for nanoparticle coating either by covalent chemistry or through physical adsorption involving weak interactions. This project deals with the development of stimuli-responsive hybrid nanoparticles that can offer new therapeutic strategies, combined with imaging properties, for pathologies involving the crossing through the blood brain barrier. These systems are built around a magnetic core based on perovskite, with a Curie temperature tunable in the body temperature range and are able to act as contrast agents in magnetic resonance imaging (MRI) as well as heat inductors in AC magnetic fields. This inorganic core is surrounded by a thermo-responsive polymeric corona that controls the loading and the release of drugs, and can be functionalized with specific ligands ensuring the targeting specificity. Promising results on the targeting of brain inflamatory regions are presented.

COLL 44

FeCo-Graphitic carbon nanocrystals as multifunctional imaging and therapeutic agents

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Delivery of cancer chemotherapeutics has presented several challenges, including low tumor uptake, inability to monitor distribution in the body and severe side effects for the patient. To address these issues, FeCo-graphitic carbon nanocrystals are currently being developed as a multi-functional imaging and therapeutic agent. These 4 nm nanocrystals contain a metal core surrounded by a single layer of graphitic carbon. The surface of the nanocrystals is non-covalently functionalized with phospholipid-PEG rendering this material highly bio-compatible. For drug delivery, doxorubicin is loaded onto the graphitic sidewall through pi-pi stacking. The high optical absorption of nanocrystals in the near-infrared region offers possibilities for photothermal chemotherapy. *in vitro* and *in vivo* studies have shown the enhanced therapeutic effects of combining chemotherapy and photothermal heating to ~43° C. In addition to treatment, magnetic resonance imaging can be used to monitor tumor uptake and the bio-distribution of this material.

COLL 45

Protein activated near-infrared fluorescence of nanoparticles surface modified with azide terminated emitters: Applications in photodynamic therapy

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Poly(propargyl acrylate) (PA) particles were surface modified through the copper-catalyzed azide/alkyne cycloaddition of azide-terminated indocyanine green (azICG), a near-infrared emitter, and poly(ethylene glycol) (azPEG) chains of various molecular weights. The placement of azICG onto the surface of the particles allowed for the chromophores to complex with bovine serum albumin when dispersed in PBS that resulted in an enhancement of the dye emission. In addition, the inclusion of azPEG with the chromphores onto the particle surface resulted in a synergistic nine-fold enhancement of the fluorescence intensity, with azPEGs of increasing molecular weight amplifying the response. Preliminary photodynamic therapy (PDT) studies with human liver carcinoma cells (HepG2) combined with the modified particles indicated that a minor exposure of 780 nm radiation resulted in a statistically significant reduction in cell growth.

COLL 46

Hybrid plasmonic-magnetic, non-toxic biomarkers

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Hybrid plasmonic-magnetic nanoparticles possess properties that are attractive in bioimaging, targeted drug-delivery, *in-vivo* diagnosis and therapy. The stability and toxicity, however, of Ag nanoparticles challenge their safe use today [*Adv. Funct. Mater.*, in press, *2010]*. Here, non-toxic, SiO_2-coated, Janus-like Ag/Fe_2O_3 nanoparticles are prepared by flame technology as demonstrated with *E. coli* and bovine serum albumin. A nanothin hermetic SiO_2 shell around these bifunctional nanoparticles leaves intact their magnetic-plasmonic properties but prevents the toxic Ag^+ ions release [*Environ. Sci. Technol., 2010, **44**:5649*] from nanosilver surface and its direct contact with live cells. Furthermore, this silica shell reduces the interaction among iron oxide particles and hinders their flocculation in aqueous suspensions. As a result, these hybrid particles exhibited no cytotoxicity and remained stable in suspension with nosigns of agglomeration and sedimentation. Their performance as biomarkers was explored by selectively binding them with live tagged raji cells enabling their detection and magnetic manipulation.

COLL 47

Evaluation of multifunctional human serum albumin magnetic nanoparticles for drug delivery and biomedical imaging

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Nanoparticles have gained considerable interest as promising drug delivery agents. In this study, we report the synthesis and characterization of multifunctional human serum albumin magnetic nanoparticles for potential drug delivery, biomedical imaging, and therapeutic applications. Characterization of the nanoparticles using dynamic light scattering and transmission electron microscopy shows well dispersed, spherical nanoparticles with average diameter of around 160 nm. Various drugs and magnetic nanoparticles could be efficiently incorporated into these human serum albumin nanoparticles. For instance, dopamine and magnetic nanoparticles have simultaneously been incorporated into these human serum albumin nanoparticles, and dopamine release using collagenase enzyme has been demonstrated. This result suggests great potential for using this nanoparticle system for drug delivery to tumors where such matrix metalloproteinases are over expressed. The presence of magnetic nanoparticles

offers the possibility of using these nanoparticles for magnetic resonance tissue imaging, magnetic triggered drug release, and magnetic hyperthermia therapy.

COLL 48

In vivo imaging and tumor targeting using a plant virus nanoparticle

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Plant virus nanoparticles (PVNs) derived from the Red clover necrotic mosaic virus have been developed as imaging and tumor targeting agents. The capsid consists of 180 proteins in an icosahedral shell that can be loaded with chemotherapeutic agents and functionalized with fluorophores and targeting peptides. The PVN is shown to be a live-imaging agent in a murine model. Shrinkage of a melanoma tumor is also shown in a murine model using a doxorubicin-loaded PVN with a N-Cadherin targeting peptide.

COLL 49

Plasmon resonant liposomes for targeted delivery to cancer cells

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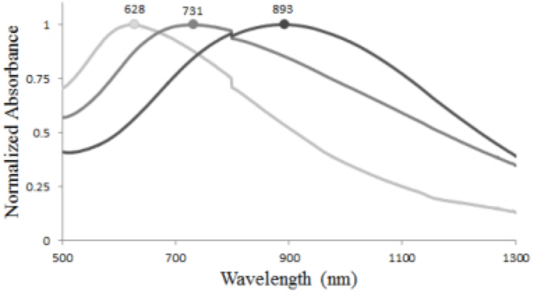
We demonstrated formation of plasmon resonance by deposition of gold on the traditional temperature sensitive liposomes (Au-TTSL). Reduction of gold chloride by citric acid in the presence of liposomes results in the formation of 100 nm diameter plasmon resonance structures with resonance between 600 and 1000 nm, shown below. Au-TTSLs release their content when illuminated at the wavelengths matching the plasmon resonance position. These biodegradable Au-TTSLs are capable of targeted delivery and spectrally multiplexed release of therapeutic or diagnostic agents.



COLL 50

Multifunctional mesoporous nanoparticles for targeting, imaging and drug delivery

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Mesoporous silica nanoparticles (particle diameter ~ 100 nm, pore diameter ~ 2 nm) are derivatized with molecules designed to induce multiple functionality. The functions highlighted in this talk include incorporation of smaller metal nanocrystals (for magnetic activation), targeting molecules towards specific cells with surface coatings, fluorescence (for imaging), and most importantly, molecules that undergo large amplitude motion (nanomachines) in response to specific stimuli and can trap molecules in the pores and release them on command or in response to interactions with cells [1,2]. Two classes of nanomachines that are based on molecules that undergo large amplitude motion when attached to mesoporous silica are described: impellers and valves. Derivatized azobenzene molecules attached to the interior pore walls function as impellers that can move other molecules through the pores. Rotaxanes and pseudorotaxanes, placed at pore entrances, function as gatekeepers or valves that can trap and release molecules from the pores when stimulated. Six methods of valve actuation have been demonstrated to date: redox, light, pH, metal ions, enzymes and magnetism. Examples of the machines and their operation *in vitro* and *in vivo* will be presented. [1] M. Liong, S. Angelos, E. Choi, K. Patel, J.F. Stoddart and J.I. Zink, *J. Mater. Chem.*, **19**, 6251-6257 (2009) [2] H. Meng, M. Liong, T. Xia, Z. Li, Z. Ji, J.I. Zink and A.E. Nel, *ACS Nano*, 4, 4539-4550 (2010)

COLL 51

Cationic glyconanoparticles for gene delivery

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The use of nanomaterials for biological applications is an emerging field of research, which seems promising towards many biological applications including gene delivery. A variety of nanomaterials of various shapes have been synthesized and utilized for different biological applications. Gold nanoparticles and carbon nanotubes are examples of nanomaterials which are unique due to their physiochemical and biomedical properties. However, the passivation of these nanomaterials by suitable ligands is required for their stability in

physiological conditions and for their use in biomedical applications. For this purpose, well-defined cationic glycopolymers are first synthesized by the reversible addition fragmentation chain transfer (RAFT) process and their cytotoxicity is determined. The cationic glycopolymer coated gold nanoparticles of varying sizes, and carbon nanotubes were then produced by surface functionalization methods to obtain monodisperse gene deliver agents. The nanomaterials thus obtained were subsequently used for transfection purposes in human cell line. The study of transfection efficiencies of gold nanoparticles as a function of core diameter of gold nanoparticles showed that size of gold nanoparticles significantly affect the transfection abilities of gold nanomaterials. The nanoparticles of 40 nm core diameter, showed enhanced gene transfection efficiency, when compared to the other sizes of nanoparticles. The cationic glycopolymer-*f*-SWNTs also proved to be an effective gene delivery agent with reduced toxicity. The transfection efficiency values obtained were upto 70% with considerably reduced toxicity when compared to commercially available agents.

COLL 52

Elementary events underlying force generation in neuronal lamellipodia

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By using optical tweezers, we have characterized force generation in neuronal filopodia and lamellipodia with a nanometer sensitivity and sub-millisecond temporal resolution. Filopodia of dorsal root ganglia neurons exert forces up to 2 pN, while hippocampal neurons exert larger forces up to 4-6 pN. When lamellipodia of DRG or hippocampal growth cones grow pushing an optically trapped silica bead, forward and backward jumps of 2-20 nm are detected. When lamellipodia retract, pulling the beads with them, no jumps are observed. Frequency and amplitude of these events were reduced by 25 nM Jasplakinolide, a blocker of actin filament depolymerisation known to reduce actin turnover. Our results identify the elementary events underlying force generation and show that protrusion is not a smooth mechanism in which actin molecules are added one by one, continuously, but it is a discontinuous process in which bursts of actin polymerization and depolymerization alternate.

COLL 53

Molecular interactions between model cell membranes and biological molecules

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Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular interactions between model cell membranes and various peptides and proteins. Antimicrobial peptides with alpha-helical, 3-10 helical and beta-sheet structures were studied, including melittin, magainin 2, MSI-78, alamethicin, and tachyplesin I. The membrane insertion behavior of cytochrome b5 and its mutants was examined using SFG in real time in situ. The membrane orientations of G(beta-gamma) and its complex with GRK2 were measured using polarized SFG spectra. SFG has been developed into a powerful tool to study membrane peptides and membrane proteins at the molecular level.

COLL 54

Single molecule binding of CD44 to fibrin vs. P-selectin predicts their distinct shear-dependent interactions in cancer

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P-selectin and fibrin(ogen) play pivotal roles in the hematogenous dissemination of tumor cells. CD44 variant isoforms, CD44v, have been identified as the major functional P-selectin ligands and fibrin receptors on metastatic colon carcinoma cells. The molecular recognition of CD44v by fibrin mediates firm adhesion at low shear, whereas CD44v-P-selectin binding supports transient rolling interactions at elevated shear stresses and low P-selectin site densities. We used single molecule force spectroscopy to provide a molecular interpretation for these two distinct adhesion events. The CD44v-P-selectin relative to the CD44v-fibrin bond has a longer unstressed equilibrium lifetime, a lower reactive compliance, and a higher tensile strength. These intrinsic differences confer the ability to the CD44v-P-selectin pair to mediate binding at higher shear stresses. Increasing the receptor-ligand contact duration (2-200 milliseconds) did not affect the micromechanical properties of CD44v-P-selectin bond, but it increased the tensile strength and the depth of the free energy barrier of the CD44v-fibrin bond and decreased its reactive compliance. This bond strengthening at longer interaction times may explain why CD44v binding to immobilized fibrin occurs at low shear and correspondingly high contact durations. Biochemical studies revealed a role for CD44v sulfation in CD44v-fibrin bond maturation. Single molecule characterization of receptor-ligand binding can predict the shear-dependent cell-substrate adhesive interactions observed *in vitro* and *in vivo*.

COLL 55

Selective protein affinity and structure transformation of domains in lipid membranes

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We engineered novel protein-lipid assemblies in lipid membranes through the design of a lipid-like molecule, 1,2-dipalmitylglycero-3-trioxanonyliminodiacetic acid (DPIDA), endowed with tail-driven affinity for specific domains and head-driven affinity for proteins at the membrane surface. When included in giant vesicles composed of DPPC, cholesterol, and diphytanoylphosphatidylcholine (DPhPC), DPIDA partitioned to domains of the ordered phase (solid or liquid depending on vesicle composition). With Cu(II) present, his-tagged proteins show specific affinity for the ordered lipid domains through coupling interaction between the histidine residues and Cu(II)-IDA complexes positioned at the membrane surface. Steric pressure from the crowding of surface-bound proteins resulted in transformation of the domains into lipid tubules having persistence lengths that depended on their phase state. These results demonstrate the ability to direct morphology of self-assembled membrane structures via tuning of membrane composition and ligand affinity.

COLL 56

Transport of hydrophobic molecular ions through living cell membrane: Effects of membrane structure and solvent ionic strength

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Using the nonlinear optical phenomenon – Second Harmonic Generation, which enables differentiation between molecules adsorbed at the cell membrane and the ones dissolved in the solution, we are now able to make time-resolved probe of molecular transport through membranes of living biological cells. Time-resolved observations made on the transport of a modest size hydrophobic molecular ion (~ 360 Da MW) at the *E.Coli* bacteria, a cell with two membranes, and a eukaryotic cell - the Murine Erythroleukemia (MEL) cell – demonstrate the relations between the membrane structure and the transport rates. The *E. Coli* outer membrane embedded with ion channels affords a transport rate one order of a magnitude faster than that of the inner membrane which has no ion transport porins. The MEL cell membrane, which has a more tightly packed lipid structure without ion channels, appears to prohibit the transport of hydrophobic ions. The salt content of the solvent in which the biological cells reside also shows strong influence on the adsorption and transport of hydrophobic ions at the cell

membrane. In order to understand the observations made on biological cells, we have characterized the effects of ionic strength and ion specificity on the adsorption hydrophobic ions on model colloidal particles – polystyrene microparticles terminated with negative, positive or no charges. It is observed that salt ionic strength and ion specificity affect molecular adsorption depending on the nature of the molecule-surface interactions.

COLL 57

Invasive phenotype is tuned by substrate rigidity: Implications for basement membrane invasion

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Recent studies suggest that extracellular matrix (ECM) rigidity regulates cancer invasiveness, including formation of invadopodia, subcellular actin-rich protrusions associated with ECM-degrading proteinases. However, the relevant mechanical range is unclear for the basement membrane (BM) and stromal tissue environments encountered by these cells. Furthermore, it is also unclear whether cancer cell invasiveness is responsive to a narrow rigidity window or spans a broad range of substrate rigidities. In this study, we used a combined analysis of tissue-derived model BM and stromal matrices and synthetic substrates to understand the regulation of invadopodia formation and activity by substrate rigidity. Urinary bladder matrix-BM (UBM-BM) was found to be a rigid material with low and high strain elastic moduli of 8.1 and 70.0 MPa, respectively, which were larger than the values of 1.8 and 10.9 MPa for the thicker UBM that consists primarily of stromal material. Using synthetic substrates that span kPa to GPa moduli, we found a peak of invadopodia-associated ECM degradation centered at ~30 kPA. Surprisingly, we found peaks in the number of invadopodia/cell at not only 30 kPa but at 2 GPa as well suggesting cancer cells can sense much higher moduli. Overall, degradation was higher in the rigidity range that was closer to the stromal UBM; therefore, a more invasive phenotype was expected on the stroma versus the BM which was verified by invadopodia numbers on the tissue-derived scaffolds. These data suggest that there is an optimal range of rigidity for expression of the invasive phenotype and that the BM represents a rigid environment for cancer cells that can be less conducive to invasion than softer substrates such as stromal collagen.

COLL 58

Bending membranes with proteins: Lessons from cellular reconstitution

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Cells use lipid bilayers to encapsulate and compartmentalize biological molecules and chemical reactions. Growing knowledge of cellular membranes reveals that they are more than passive barriers but play an active role in many biological processes as a scaffold for organizing proteins in space and time. It is now understood that membranes are made up of many species of lipids and integral and peripheral membrane proteins. In order to understand the interplay of lipids and proteins involved in cellular functions such as endocytosis, exocytosis, and cell motility, in vitro reconstitution of purified proteins with model membranes shows great potential. However, current techniques for rebuilding membranes from purified components are limited in their ability to create conditions that emulate the physical and biochemical constraints of biological systems. We have developed an integrated method for forming giant unilamellar vesicles with control over membrane composition, asymmetry, and internal contents. This method extends our piezoelectric microfluidic jetting technique for creating giant unilamellar vesicles (GUVs) from planar bilayers, analogous to blowing bubbles from a soap film, to include control of lipids and protein composition of the membrane. We demonstrate asymmetric incorporation of physiological and functionalized lipids into inner and outer membrane leaflets and show controlled orientation of functional transmembrane proteins. We use this approach combined with traditional GUV formation techniques to advance our understanding of how membrane deformation is driven by proteins. Deformations of importance to cellular function are often characterized by regions of high curvature brought about by interactions between lipids and proteins. We examine the role of integral and peripheral membrane proteins involved in endo- and exocytosis and the role of lipid composition on protein binding.

COLL 59

Nanocomposite materials for energy applications

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Nanocrystalline materials are of interest for a variety of applications. This talk describes the design and synthesis of metallic, metal oxide and semiconducting nanocrystals of controlled size and morphology. The nanocrystalline building blocks are used to create multifunctional nanocomposites and heterodimers with

unique properties. They are successfully tailored towards energy applications, such as biomass conversion, catalytic combustion, and fuel cells.

COLL 60

Room temperature growth of anisotropic lead chalcogenide nanostructures from quantum dots for use in photovoltaics

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Owing to their facile solution phase synthesis and high processability, semiconductor quantum dots have garnered much interest for their possible use in photovoltaic devices. Many such devices have been reported, but efficiencies remain prohibitively low due in part to poor electron transport through the surfactant layer on the surface of each nanocrystal. To address this problem we propose to use core/shell nanocrystalline rods with multiple quantum confined cores for exciton generation within a rod-shaped semiconductor shell for charge transport. Toward this goal we have synthesized lead chalcogenide nanorods at room temperature by addition of long-chain fatty acids to oleic acid-capped spherical lead chalcogenide nanocrystals. The presence of additional carboxylic acid groups is presumed to promote exposure of reactive facets, thereby leading to the assemly of larger nanostructures. We aim to extend these methods to synthesize core/shell nanocrystals containing multiple absorptive cores and to incorporate them into solar cell devices.

COLL 61

Metal oxide nanotube films prepared via pulsed laser ablation for energy applications

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Recently, nanostructured materials have received greater attention for energy applications due to their distinct electrical and chemical properties, especially in photovoltaic and energy storage devices, which require very high surface areas and energy densities. The fabrication of 1D semiconducting metal oxide nanostructures plays a crucial role in developing alternative energy storage/ conversion devices with high power and energy densities. Low dimensional nanotubular morphologies are particularly attractive, but the preparation of thin films remains a challenge. A novel technique for the preparation of TiO_2 and V_2O_5 nanotube films via pulsed laser deposition (PLD) will be described. A high

energy laser beam (248 nm) was demagnified on a metal oxide target, depositing a thin film on the substrate. After PLD a simple hydrothermal treatment was used to grow the nanotubes. High surface area small diameter (<10 nm) TiO_2 nanotube (TNT) thin films were grown on stainless steel and Ti foils and then sensitized with dyes and PbS quantum dots. Photovoltaic results using the TNT films will be discussed. V_2O_5 nanotubes (VNT) (~50 nm) were prepared on high surface area carbon fiber sheets via the pulsed laser deposition technique. Coin cell type (CR2032) capacitors were assembled with the VNT coated carbon as one electrode and carbon as the other. Capacitance and power density results will be presented. The nanotube films were characterized by TEM, SEM, XRD, FTIR and Raman spectroscopy.

COLL 62

Templating synthesis of hollow TiO_2 shell nanostructure with crystallinity

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Hollow TiO_2 shell nanostructures are usually synthesized through templating-derived synthetic methods. These methods could mostly allow the formation of amorphous and hollow TiO_2 shell structures. For practical applications (e.g. photocatalysis and solar cells), it should have the improved crystallinity via post-treatments such as a calcination and/or hydrothermal treatment. However, these post-treatments lead to breakage of the shell and formation of large TiO_2 crystalline grain. In this work, we report a preparation method of hollow TiO_2 shell with anatase crystalline structure through a sol-gel derived templating method and a sequential silica-protected calcination. The TiO_2 shell layer with nano-sized thickness was coated on the colloidal silica core particles (SiO_2@TiO_2) and the resulting core-shell nanostructure was encapsulated by additional silica layer as a protecting layer. After calcination and etching, TiO_2 had anatase crystalline structure while maintaining the hollow shell structure with nanosized thickness. The outside silica layer is supposed to act to prevent growing TiO_2 grain which can lead to breakage of shell during calcination at high temperature. We will discuss further our synthetic methodologies for hollow TiO_2 shell nanostructure with crystallinity in this presentation.

COLL 63

Morphology control of nanocrystals with biomolecules

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The physical and chemical properties of nanocrystals (NCs) strongly depend on their sizes and morphologies. One notable example is that noble metal NCs of various shapes have been reported to demonstrate different catalytic properties as a result of the distinct crystallographic facets displayed on the NC surfaces. Here we demonstrate the utilization of facet-specific peptide sequences as regulating agent for predictable synthesis of platinum nanocrystals with various morphologies in aqueous solution at room temperature. Specifically, Pt-{100} and Pt-{111} binding peptide sequences are identified against Pt-{100} faceted and Pt-{111} faceted substrates through a biomimetic evolution process. Importantly, these facet-specific peptides can be readily used to direct the growth of Pt nanocrystals in a highly predictable manner. The Pt-{100} binding peptide produces cubes enclosed by six {100} facets and the Pt-{111} binding peptide produces tetrahedrons enclosed by four {111} facets, as expected. Furthermore, we demonstrate that a shape transformation from cube to tetrahedron can be achieved by switching from {100} binding peptide to {111} binding peptide in the solution. These studies demonstrate unambiguously the abilities of the facet selective binding peptides in determining the nanocrystal shapes, presenting a critical step forward in exploiting biomolecules for programmable synthesis of nanostructures.

COLL 64

Counting the atoms in supported, monolayer-protected gold nanoclusters

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Size-selected atomic clusters can be used as novel mass standards to “weigh” other nanoparticles, via quantitative high angle annular dark field imaging in the scanning transmission electron microscope (HAADF-STEM). We apply this “atom counting” method to the problem of monolayer-protected Au38 (MP-Au38) clusters – do they really contain 38 Au atoms? We co-deposit size-selected Au clusters and MP-Au38 nanoparticles on the same TEM grid. Quantitative analysis shows the MP-Au38 cluster intensity correspond to 47 Au atoms, but once the contribution due to the ligands is calibrated, they contain 38 ± 2 Au atoms. The detailed atomic structure of the MP-Au38 clusters was also investigated, a special challenge given the instability of such small clusters under the electron beam. Serial-acquisition of images at high speed (0.2s/frame) shows many clusters have an elongated shape, with an aspect ratio up to ~1.4, confirming the theoretically predicted preference for a prolate structure.

COLL 65

Anisotropic palladium nanocrystals as promising electrocatalysts

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We report here a facile PVP-assisted chemical reduction process for preparation of various palladium (Pd) nanocrystals including nanoplates, octahedrons, porous nanocrystals, and hollow nanocrystals. The synthesis involved only the use of PdCl2 as the precursor, PVP as the reducing and stabilizing agents, and a specific salt like NaCl or NH4OH as the additive. By modulating the relevant reaction conditions such as the amount of PdCl2, the amount of additive, and the reaction temperature, we were able to obtain anisotropic Pd nanocrystals with controllable morphologies. As compared to the commercial Pd nanoparticles, the four types of Pd anisotropic nanocrystals all exhibited superior electrocatalytic activities toward hydrogen adsorption/desorption, revealing their catalytic potential in relevant electrochemical reactions. Furthermore, among the four Pd samples, hollow nanocrystals possess the highest current density of formic acid oxidation and the largest If/Ib ratio, demonstrating that they could be promisingly used as highly-efficient CO-resistant electrocatalyst in the direct formic acid fuel cell.

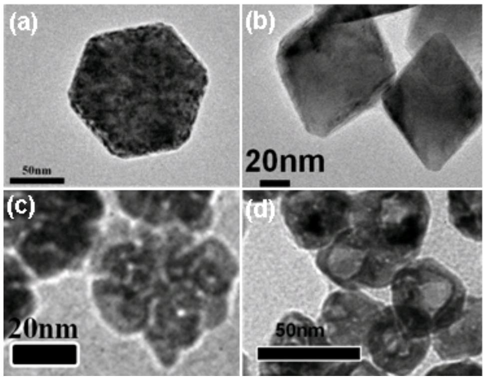

Figure 1. TEM images of the as-synthesized anisotropic Pd nanocrystals: (a) nanoplates (b) octahedrons, (c) porous and (d) hollow nanocrystals.

COLL 66

Electrochemical control of the self-assembly of redox-active surfactants within microfluidic channels

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This presentation will describe an investigation that combines the use of redox-active (ferrocenyl) surfactants and electrochemical methods to achieve spatial and temporal control of surfactant assemblies formed within microfluidic channels. Fundamental issues related to the dynamics of self-assembly as well as mass transport of surfactant assemblies in microfluidic systems will be addressed. The ability to electrochemically generate spatially localized populations of micelles within microfluidic channels, and also realize lateral, steady-state gradients in the concentration of surfactants across microchannels, will be described. Finally, electrochemical control of surfactant concentration gradients within microfluidic channels will be shown to offer the basis of a new means to generate lateral gradients in the chemical potential of a range of solutes, thus leading to solute-specific partitioning across microfluidic channels.

COLL 67

Surfactant adsorption timescales in microfluidic droplet formation

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Surfactants are significant in the formation of emulsion droplets. In microfluidic devices, surfactants lead to “tipstreaming” of micron-scale droplets at specific concentrations and flow rates. In this process, surfactant adsorption competes with convection to determine the local surface concentration and interfacial tension, and therefore the ability to draw thin threads. We dissolve nonionic CiEj surfactants in water and generate droplets in a microfluidic flow focusing device. By varying hydrophobic tail length, we show that tipstreaming occurs only when adsorption is rapid enough for surfactant to adsorb but viscous stresses are strong enough to maintain a surface tension gradient. The experiments indicate that the allowable surface coverage for tipstreaming is very small, even though the bulk surfactant concentration is greater than the critical micelle concentration. We use a 1D kinetic-limited transport model to demonstrate that small surface coverages can lead to highly nonlinear effects like tipstreaming at these length and time scales.

COLL 68

Diffusion in evaporating solutions

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We present an analysis of the colloidal dynamics of particles in a mixture of two solvents subjected to evaporation. For simplicity, only one out of the two solvents is considered to be volatile. The evaporation generates a distribution of the solvent concentration in the system. As the particles selectively interact with the solvents, their migration becomes affected by a “chemotaxis” force, caused by the gradient in the solvation energy along the diffusion path. The net particle flux is the result of the interplay between the migration under the action of the chemotaxis and the bulk convection flow caused by the evaporation. The most unusual features of the particle migration occur when the particles have an affinity to the evaporating solvent. In this case, the particles may diffuse against the concentration gradient and form bands with increased particle concentration, i.e., undergo focusing. The resulting particle concentration patterns are strongly dependent on the geometry of the container in which the evaporation occurs. This model has important practical applications. It provides a framework for understanding and controlling the skin formation at the surface of evaporating colloidal suspensions, an effect that is briefly illustrated experimentally on the example of ink-jet printing. On a thermodynamic level, the model is also applicable to cases, in which the third component is molecularly dispersed, although a smaller magnitude of the effects is predicted.

COLL 69

μ^2rheology: High-throughput microrheology in microfluidic devices to screen a large material composition space

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High-throughput microrheology combines the use of microfluidic devices and passive microrheology to enable the characterization of material rheology over a large composition space, while minimizing both the quantity of sample and sample preparation time. This enables materials discovery and characterization, specifically of scarce and rare materials. Within the microfluidic device, distinct samples with uniformly varying compositions are separated by an immiscible fluid. Rheological properties of each sample are measured using multiple particle tracking microrheology. We demonstrate the power of this approach using a covalently cross-linked hydrogel designed for therapeutic applications. Gelation state diagrams compiled from hundreds of microrheological samples yield the compositions in which gelation occurs as a function of total polymer concentration, number of active sites for cross-linking on the gelling molecule, and molecular weight of the cross-linking molecule. Using these state diagrams, specific hydrogel compositions selected for their weak gel properties are chosen to effectively process the hydrogel into nanofibers using electrospinning. This demonstrates the capabilities of microrheological screening to identify material properties of engineering interest while minimizing the amount of material and time for rheological characterization.

COLL 70

Imaging amperometry

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The ability to measure local electrochemical current density is important to a number of applications including the high throughput evaluation of electro-catalysts and corrosion studies. We present a technique called imaging amperometry that measures local current density via the response of probe particles near a working electrode. Single particle longitudinal (ie. vertical) and multi-particle lateral motion is a function of the intensity and direction of local current density. This presentation will focus on single particle vertical motion. Measurements are conducted using an Electrochemical Total Internal Reflection Microscope (ETIRM) that combines techniques traditionally found in colloid science (TIRM) and electrochemistry (cyclic voltammetery). We demonstrate this technique using a continuous indium tin-oxide (ITO) thin film electrode, a discontinuous ITO thin film electrode, and a continuous (but electrochemically patchwork) ITO/gold thin film electrode. In all cases, we are able to measure local electrochemical activity by monitoring the scattered light intensity from the particle.

COLL 71

Coalescence on command: Electrically modulated partial coalescence of oppositely charged drops

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Oppositely charged drops fail to coalesce above a critical field strength, despite the attractive force between opposite charges[1]. Here we report a technique to externally control the extent to which charged droplets are allowed to coalesce. For sufficiently low conductivities, the degree of coalescence of water drops in oil

depends sensitively on the applied field strength and droplet charge. Strikingly, in this regime the size of the daughter droplet is independent of the drop conductivity. We present evidence that the charge transfer is instead dominated by convection during the capillary-driven penetration of a vortex into the larger drop. Moreover, we demonstrate that the observed daughter droplet size accords with a model based on a balance between capillarity and electrostatic repulsion. The results presented here should affect our understanding of any process involving charged liquid drops, including de-emulsification, atmospheric conduction and lab-on-a-chip manipulations. [1]Ristenpart *et al.*, *Nature* **461**, 377 (2009).

COLL 72

Electrokinetic locomotion by reaction induced charge auto-electrophoresis

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The controlled motion of synthetic nanoscale motors may represent a major step towards the development of practical nanomachines, artificial cells, and autonomous microsystems. We are investigating locomotion of bimetallic synthetic nanomotors that, analogous to their biological counterparts, harvest chemical energy from their local environment and convert it to useful work. Bimetallic nanorods can autonomously propel themselves at a hundred body lengths per second through aqueous solutions by using hydrogen peroxide as a fuel. We can control the motion of nanomotors using magnetic fields and chemical species to control the motion of Pt-Ni-Au nanorods. Several arguments have been proposed to describe the physics underlying their locomotion, but there is no detailed theory on the propulsion mechanism. We are simulating the physics of rod-shaped nanoparticles with asymmetric surface fluxes. Our models show that locomotion is driven by electric body forces in the fluid that arise due to finite space charge and internally generated electric fields surrounding the rod. The electric fields and charge density are generated by dipolar cation fluxes, such as those generated by heterogeneous electrochemical reactions with broken symmetry. We present a set of governing equations, a scaling analysis, numerical simulations, and experiments that describe the physics underlying the autonomous motion of electrocatalytic bimetallic nanomotors due to a mechanism we call Reaction Induced Charge Auto-Electrophoresis (RICA).

COLL 73

Electrospinning as an X-ray source

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Nanofibrous materials, e.g. electrospun fibres and jets, consist of midget cylindrical structural features with diameters ranging from several nanometers up to several tenths of a micrometer. Tiny nanofibres and electrospinning jets can serve as unusually fine electrodes to create extremely high electric field intensity in their vicinity. Here we report on the discovery that electrically charged polymeric jets in contact with ambient atmospheric air generate X-ray beams up to energies of 20 keV. We also hypothesize how gigantic field strength values are created and how they accelerate ions under atmospheric conditions. Experimental set-ups designed by us for the generation of high energy electromagnetic radiation are extremely simple consisting of unsymmetrical capacitors with at least one electrode made by nanofibrous material.

COLL 74

Probing the insides of live cancer cells with targeted nanoparticle sensors

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Biocompatible targeted nanoparticle sensors have been applied for studying the chemistry and physics at selected locations inside live cells, such as brain cancer cells. They have been applied to a large range of chemical species (ions, radicals, molecules) and to physical parameters such as electric field and viscosity. These nanosensors use molecular targeting so as to enter specific cells or specific locations inside the cell. The targeting is achieved by the use of peptides, antibodies, etc. Of special interest to oncology are sensors that measure pH, various ions, reactive oxygen species, etc. The advantage of nanoparticle sensors over naked molecular probes include: easy targeting ability, better biocompatibility, immunity to perturbations by cell components, and controlled distribution at the cell location of interest. It is also possible to use Magnetically MOdulated Optical Nanosensors (MagMOONs), which enable to reduce the effects of autofluorescence by 3-4 orders of magnitude. The sensor matrix may be polymeric (hydrogel), glassy (silica), or a combination (ormosil). The size of the nanosensors (20-200 nm) may be controlled by emulsion or reverse emulsion preparation methods. Towards application of such sensors in-vivo, preliminary work has shown the feasibility of photo acoustic nanosensors, where the chromophores play the role of “sonophores”. For instance, highly selective and sensitive measurements of oxygen and its reactive and unstable products are crucial to the biomedical sciences and especially to studies of cancer and its treatment. The first reliable measurements of oxygen distribution

among cell compartments were carried out with an infrared nanoPEBBLE (photonic explorer for bioanalysis with biologically localized embedding) with targeting ability. The short lived species of H_2O_2 (hydrogen peroxide) and singlet oxygen (activated or excited species of oxygen) have also been detected selectively with the help of nanoPEBBLEs, where not only the matrix but also the size is crucial for its selective detection.

COLL 75

Tethered growth factor gradients for directing stem cell function

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Immobilized peptide fragments have been shown to exhibit different bioactivity from soluble growth factors to regulate cell behaviors. To better understand these differences and optimize ligand conditions for directing cell function, a versatile surface gradient platform, which possess continuous concentration variations along a single substrate, is employed to illustrate the immobilized ligand density effects on the cell differentiation. The gradient method enables the acceleration of the screening and discovery of phenomena, by lowering the number of experiments dramatically, and also the reduction of methodological error, facilitating the systematic studies of optimal peptide concentrations for cell regulation.

COLL 76

Particles of controlled size, shape and chemical functionality for probing biological processes

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In 1965, Gordon Moore described that the number of components in integrated circuits had doubled every year since 1958. This trend has continued, enabled by advances in photolithography. The minimum feature size of transistors has decreased from about 10 microns in 1970 to 0.045 microns today. As such, this top-down nano-fabrication technology from the semiconductor industry is now relevant for the design of medicines and vaccines. This lecture will describe the design, synthesis and efficacy of organic nano- and micro-particles using a top-down nano-fabrication technique called PRINT (Particle Replication in Non-wetting Templates). PRINT is a continuous, roll-to-roll, high resolution molding technique that allows the fabrication of precisely defined micro- and nano-particleswith control over chemical composition, size, shape, deformability and

surface chemistry. Examples to be described include the design of PRINT particles useful as vaccines (influenza, H1N1, pneumo), targeted chemotherapy agents, anti-bacterials, and even an entirely new class of inhalation therapeutics.

COLL 77

Biomolecular analysis using surface-driven ordering transitions in liquid crystals

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This presentation will address the development of new molecular analysis tools to identify and validate biological endpoints whereby the activity of novel anti-cancer agents can be more accurately and rapidly evaluated as to their molecular mechanism(s) and clinical relevance. The work is focused on epidermal growth factor receptor (EGFR), given that its overexpression and mutation has been closely-associated with some of the most incurable cancers. In particular, the presentation will address the design of chemically functionalized and nanostructured surfaces that permit detection of EGFR, and lipid assemblies (native microvesicles) that contain EGFR, using ordering transitions in thermotropic liquid crystals. The approach exploits the exquisite surface-sensitivity of the ordering of liquid crystals, and more broadly, the use of liquid crystals to amplify molecular transformations at surfaces into ordering transitions that occur on optical scales. In the long term, these new, surface chemistry-based tools should be useful for the assessment of the molecular mechanisms and consequences of anti-cancer agents, thereby facilitating their research from basic biology through to clinical assessment of efficacy.

COLL 78

Nano mechanical and spatial manipulation and characterization of cell surface receptors

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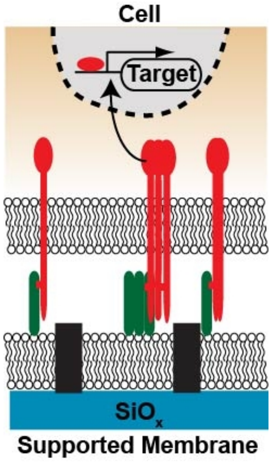
Cell survival depends on the accurate recognition and response of surface receptors to their immediate chemical environment. The homo- and hetero-association of membrane receptors at multiple length scales is believed to be a

key step in the initiation of biochemical signals. For example, the receptor tyrosine kinase ErbB2, which is overexpressed in 20-30% of breast cancers, can be activated by clustering with other ErbB family receptor proteins or through overexpression-driven oligomerization. We investigate the existence and importance of large scale (from 10 nm to 1 micron in scale) receptor associations in living cells using nanopatterned synthetic interfaces. A suite of bottom-up and top-down nanofabrication techniques are used to tailor supported lipid membranes that are decorated with specific ligands. Signaling outputs are measured using a range of bioanalytical tools in order to quantify cellular response. The results of these investigations will be presented in the context of the ErbB signaling pathways in cells known to overexpress the receptor.



COLL 79

Modulation of lipoplex physicochemical properties and surface chemistry to enhance and target genetic material delivery to malignancies

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Gene therapy revealed recent successes, but its ability to revolutionize therapy depends on finding efficient vectors for genetic material delivery, devoid of immunogenicity and mutagenicity. Self-assembled synthetic vectors based on cationic lipids constitute an alternative to viral vectors but their efficiency must be improved by adapting their supra-molecular structure to extracellular and intracellular delivery barriers. We will present our synthetic and formulation approaches to cationic lipid-based gene delivery systems, correlating the nature, physicochemical and supra-molecular properties of lipid assemblies with transfection efficiency and cytotoxicity of their nucleic acid complexes. We'll emphasize the impact of size, curvature, surface charge, composition, and fluidity of lipoplexes on the above-mentioned biological properties against a wide variety of tumor cell lines (lung, breast, colon, prostate carcinomas), revealing the

most efficient formulations for each type of tumor. Our synthetic strategies to enhance targeting and internalization via lipoplex decoration with tumor specific ligands will also be presented.

COLL 80

Dynamic electrochemical control of peptide structure on surfaces

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A method is described that combines two well-known click reactions, an 'electrochemical click' reaction mediated by quinone/oxime conjugation and azide/alkyne Huisgen cycloaddition, for dynamic electrochemical control of biomolecule presentation on self-assembled monolayers (SAMs) on gold. Dynamic Arg-Gly-Asp (RGD) ligands containing terminal alkynes and oxyamines were constructed via solid phase peptide synthesis (SPPS) and immobilized to a bifunctional SAM presenting azide and hydroquinone moieties for switchable control of peptide structure. On SAM surfaces, cyclized RGD increased cell adhesion diameter and decreased cell migration rates compared to the linear form of RGD. Application of the method for an electrochemical hide and reveal is shown with an elongated RGD peptide, which adhered cells only in revealed linear form. These are the first experiments to demonstrate dynamic control of small molecules for modulating cell adhesion and migration.

COLL 81

Fibronectin-mimetic peptide-amphiphile nanofiber gels support increased cell adhesion and promote ECM production

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The design of nanofiber scaffolds has been a key objective in tissue engineering as they structurally mimic the natural extracellular matrix (ECM) found in tissues. The continous cross talk between cells and the surrounding matrix ligands plays a crucial role during development and wound healing which leads to tissue regeneration and repair. In an attempt to provide a nanofiber scaffold with a ligand that can promote cell adhesion and ECM production, we propose the use of our peptide-amphiphile nanofibers as a potential scaffold for tissue engineering. A fibronectin-mimetic peptide sequence containing both the cell-binding GRGDSP domain and the synergistic PHSRN domain has been recently developed in our group. It has been shown to be a specific ligand for the $\alpha_5\beta_1$ integrin, and has been synthesized to a C_{16} single-tailed peptide-amphiphile, PR_g (with a peptide headgroup of GGGSSPHSRN$(SG)_5$RGDSP). The PR_g peptide-amphiphiles self-assemble into nanofibers in an aqueous environment and form hydrogels. In this study, the PR_g hydrogels were characterized with cryo-scanning electron microscopy (cryo-SEM) and rheology measurements, and their surfaces were evaluated in terms of sustaining long term human umbilical vein endothelial cell (HUVEC) adhesion and proliferation, cytoskeleton formation, and secretion of extracellular fibronectin. PR_g gels were compared to polyethylene glycol (PEG) gels, PEG gels functionalized with fibronectin as well as commercially available peptide hydrogels (PuraMatrix). Our results show that the PR_g hydrogels outperform the other gels evaluated in this study and therefore hold promise as scaffolds for tissue engineering.

COLL 82

Maleimide photopatterning for probing protein-protein interactions on artificial membranes and live cells

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Functional immobilization and lateral organization of proteins into micro- and nanopatterns is an important prerequisite for miniaturizing analytical and biotechnological devices. Here we present novel and versatile approaches for micropatterning of proteins, artificial membranes and live cells based on maleimide photochemistry. The patterning strategy was carried out on glass substrates exploiting a poly(ethylene glycol) (PEG) polymer layer as a biocompatible scaffold. The flexible PEG cushion ensured specificity of the attachment of proteins and membranes, as well as the adhesion of cells. The versatility of this method is demonstrated by means of different orthogonal chemistries using covalent- and affinity-based interactions for proteins immobilization. Surfaces functionalized with alkyl-chains were utilized to obtain fluid patterned membranes into which membrane proteins were successfully reconstituted. A similar approach was used for micropatterning of transmembrane proteins in surface adhered live cells. Moreover, micropatterned functionalized surfaces were employed for selectively capturing intracellular proteins directly from adhering cells.

COLL 83

Theory of equilibrium and non-equilibrium hydrophobic effects

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General principles and underlying theory of hydrophobic effects will be described. Most important are the effects of water-density fluctuations, which play a central role in nano-scale forces of assembly. Several recent applications will be presented.

COLL 84

Wetting of nanostructured surfaces

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Wetting phenomena on nanostructured surfaces are important in materials science and biology. This lecture will describe some of our recent progress in predicting and understanding the effects of nanopatterning on topologically or chemically heterogeneous surfaces on wetting.

COLL 85

Hydrophobicity of proteins and interfaces: Insights from density fluctuations

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Water drives many biological and colloidal self-assembly phenomena including protein folding, and micelle and membrane formation, to molecular recognition. Hydrophobic interactions are frequently implicated as one major factor in these self-assembly processes. Macroscopically, hydrophobicity is often characterized by measuring droplet contact angles. Such measurements are, however, not feasible on nanoscale surfaces of proteins or nanoparticles. How does one then characterize hydrophobicity/philicity of such interfaces? We present results from theory and simulations of hydration of a variety of surfaces to connect the behavior of water at the nanoscale interfaces and surface hydrophobicity. Specifically, we show that water density fluctuations provide a quantitative characterization of the interface hydrophobicity. Density fluctuations are enhanced at hydrophobic interfaces and suppressed near hydrophilic ones. Simulations also show how properties of water at interfaces influence solute binding, folding, and dynamics of flexible molecules at interfaces. I will

demonstrate that this new perspective on hydrophobicity provides a tool for characterization of hydrophobicity patterns on protein surfaces, which are relevant for binding, recognition, and aggregation.

COLL 86

Surface nanobubbles: Phase space and evidence from molecular dynamics

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We present our recent results on surface nanobubbles. First, we have systematically investigated the occurrence of surface nanobubbles on a hydrophobised silicon substrate for various different liquid temperatures and gas concentrations, which we controlled independently. We found that nanobubbles occupy a distinct region of this phase space, occurring for gas concentrations of approximately 100%-110%. Below the nanobubble phase we did not detect any gaseous formations on the substrate, whereas micropancakes}(micron wide, nanometer high gaseous domains) were found at higher temperatures and gas concentrations. Next, we present MD simulations of surface nanobubbles which show both gas outflux and gas influx, giving support for the recently proposed dynamical equilibrium theory for nanobubble stabilization.

COLL 87

Nanobubbles at solid-water interfaces

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We have established a solvent exchange protocol to produce nanobubbles at solid-water interfaces. Here we report that the same protocol was capable of inducing gaseous micropancakes as well as nanobubbles on crystalline surfaces of highly ordered pyrolytic graphite (HOPG), molybdenum disulfide (MoS_2) and talc in water. In contrast, the same protocol was unable to induce spherical-cap shaped nanobubbles or gaseous micropancakes on amorphous (glassy) carbon or on trimethylchlorosilane coated silicon surfaces which had a similar contact angle of water as crystalline surfaces. It appears that formation of these interfacial gaseous states required adequate nucleation sites on the surfaces in addition to local supersaturation of gases. We have also investigated the influence of nanobubbles on the surface forces and bubble attachment on solid surfaces by colloid probe AFM. The forces between a carbon sphere and HOPG

surface were measured in ethanol aqueous solutions. A long-range attractive interaction was observed in ethanol aqueous solutions with less than 60 % ethanol on a volume basis. The magnitude and the range of the attractive interaction decreased with an increase in ethanol concentration in solution. An air bubble was found to attach to the HOPG surface in solutions with an ethanol concentration less than 20 volume %. The presence of nanobubbles at the HOPG surface, produced by solvent exchange and confirmed through in-situ imaging, extended the range of both the long-range attraction and the bubble attachment regime to ethanol concentrations less than 60 volume %. Contact angle analysis for ethanol-aqueous solutions in air showed that an angle of greater than 40° was required to induce a long-range attraction, modelled in this case as a capillary cavitation force. The data clearly shows that surface nanobubbles are not critical to the development of a long range attractive force and bubble pick up on surfaces or enhanced suspension rheology, but that their presence greatly aids these processes.

COLL 88

Morphology of air nanobubbles trapped at superhydrophobic nanopattened surfaces

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We study the details of air nanobubble trapping at the interface between water and a nanostructured hydrophobic silicon surface fabricated by diblock-copolymer lithography. The surface is composed of hexagonally packed hydrophobic cavities of width ~ 20 nm and depth ranging from 20 to 165 nm. Transmission small-angle X-ray scattering (SAXS) measurements show stable trapping of air nanobubbles inside the cavities with a partial water penetration of 5−10 nm into the pores, independent of the pore depth. This behavior is explained by consideration of capillary effects and the cavity geometry. For cavities of parabolic shape, the liquid can reach a thermodynamically stable configuration—a nearly planar nanobubble meniscus—by partially penetrating into the pores. This microscopic picture correlates very well with the observed increase (~20 degrees) of hydrophobicity of the patterned versus smooth surface. Moreover, we find that superhydrophobic surfaces are obtained by increasing the diameter of the etched cavities to the point they start to coalesce (diameter ~ 50 nm). Differently from the case of isolated cavities, SAXS measurements indicate that water does not penetrate into the resulting nanotexture.

COLL 89

Spontaneous formation of water droplets at oil-hydrophobic solid interfaces

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This presentation will describe the unexpected observation of spontaneous formation of micrometer-sized water droplets within micrometer-thick films of a range of different oils that are supported on hydrophobic surfaces and immersed under water. Confocal microscopy establishes that the droplets nucleate from the surface of the hydrophobic solid. A simple thermodynamic model based on macroscopic interfacial energetic arguments, however, fails to account for the spontaneous formation of the water droplets. A series of measurements do establish that the charge of the interface is important in promoting the partitioning of water to the interface. Also, the inhibitory effect on droplet formation of both salt (NaCl) and sucrose indicate that both solutes prevent partitioning of the water to the interface between the oil and supporting substrates (via osmotic effects). Other insights into the factors that influence the spontaneous formation of the water droplets at oil-hydrophobic solid interfaces will be discussed.

COLL 90

Synthesis and properties of particle-coated emulsions

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This talk will present methods for synthesis of particle-coated drops, and will describe measurements of the properties of the drops and the rheology of emulsions stabilized by colloidal particles.

COLL 91

Dynamics of soft particles at soft interfaces

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We report on the adsorption, diffusion and interfacial rheology of thermosensitive microgel particles at a liquid interface. These PNIPAM soft particles are highly

surface active as they strongly decrease the interfacial tension [1]. At low concentration, we find that the diffusion coefficient of the adsorbed particles is consistent with the one of immersed spherical particles. At higher concentration, the particles rapidly aggregate at the interface, where diffusion is completely arrested although the bulk diffusion is not affected. Surprinsingly, active surface rheological measurements (both shear and compression) show that the interface remains very soft compared to the case of interfaces laden with hard particles. We show that the aggregation process is not driven by capillary interaction and we provide a simple method for controlling the degree of adsorption and aggregation of such particles by changing the temperature or using a cosolvant.
[1] C. Monteux et. al. Langmuir, 2010

COLL 92

Squeezing emulsions stabilized by colloidal particles and fluorescent surfactants

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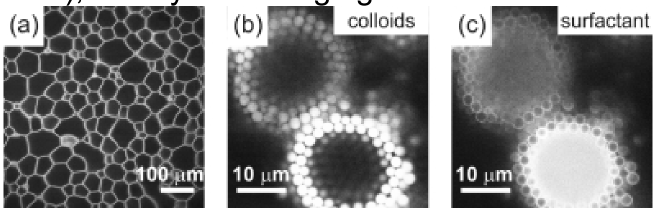
Emulsions (additionally) stabilized by colloidal particles rather than molecular surfactants alone offer superior rheological properties, which arise from a rich interplay between interfacial tension and interparticle interactions. Here, we consider particle-stabilized emulsions under centrifugal compression and reveal their structure using confocal microscopy (figure 1a). Moreover, we show that adsorption of a (fluorescent) surfactant onto the water-oil interface and onto the colloids affects the formation and structure of particle-stabilized emulsions (figure 1b/c), mainly via changing interfacial tension and particle contact angle.



COLL 93

Interfacial rheology and dynamic behavior of polymer grafted nanoparticles at the air-water interface

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Particle stabilized emulsions offer a number of advantages over traditional surfactant stabilized emulsions, however nanoparticles are less effective than colloidal particles. The binding energy of a colloidal particle is proportional to the square of the radius, so nanoparticles are less effective stabilizers. However, we see that nanoparticles grafted with polymers are particularly effective emulsifiers; stabilizing at very low weight fractions, as low as 0.003 wt% for some systems. In this work, we characterize the interfacial mechanisms that give rise to the observed efficiency and attempt to understand the key mechanism. The static and dynamic interfacial tension at air-water interfaces is measured and analyzed in terms of a simple transport model. Using an approach we have developed to study surfactant-laden air-water interfaces, we measure the interfacial elasticity through a forced sinusoidal oscillation of the interface. We present a systematic study of three grafted nanoparticle systems that form stable emulsions at the air-water interface. The results are put into the current framework of analogous surfactant studies such as dilatational elasticity and interfacial rheology.

COLL 94

Phase transitions and phonons in temperature-sensitive colloids

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Temperature-sensitive microgel particles offer new knobs for creation of novel phases and control of phase transformations in suspension. I will describe recent experiments which exploit this phenomenon to learn new condensed matter physics. In particular, colloidal particle diameter, and therefore suspension volume fraction, are readily tuned by small changes in temperature and drive melting transformations in bulk three-dimensional crystals [1], in two-dimensions wherein intermediate hexatic phases form [3], in thin crystalline films [3], and in quasi-one-dimensional cylinders [4]. Furthermore, the displacement correlation functions of such particles in glassy colloids provide new insight into the phonon modes of disordered solids in the vicinity of the jamming transition [5, 6]. [1] A.M. Alsayed, M.F. Islam, J. Zhang, P.J. Collings, A.G. Yodh, Science 309, 1207-1210 (2005). [2] Y. Han, N.Y. Ha, A.M. Alsayed, and A. G. Yodh, Phys. Rev. E 77, #041406 (2008). [3] Y. Peng, Y., Z. Wang, A.M. Alsayed, A.G. Yodh, and Y. Han, Physical Review Letters 104, 205703 (2010). [4] M.A. Lohr, A.M. Alsayed, B.G. Chen, Z. Zhang, R.D. Kamien, and A.G. Yodh, Physical Review E 81, 040401 (2010). [5] K. Chen, W.G. Ellenbroek, Z.X. Zhang, D.T.N. Chen, P.J. Yunker, S. Henke, C. Brito, O. Dauchot, W. van Saarloos, A.J. Liu, and A.G. Yodh, Physical Review Letters 105, 025501 (2010). [6] Z. Zhang, N. Xu, D.T.N. Chen, P. Yunker,

A. Alsayed, K.B. Aptowicz, P. Habdas, A.J. Liu, S. Nagel, and A.G. Yodh, Nature 459, 230-233 (2009).

COLL 95

Preferential assembly of gold nanorods on sub-100nm polymer-derived surface patterns

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The uniform arrangement of nanoscale building blocks (nanoparticles) beyond random ordering and across macroscopic length scales limits reproducible, mass production of functional devices from bottom-up concepts. Directed and self assembly concepts provide intriguing avenues to fabricate translationally-ordered nanoparticle arrangements, but lack the robustness to deliver complex spatial organization comparable to traditional lithographic-deposition concepts. The crucial challenge is to determine how to best synergize the salient features of assembly and lithography to provide fabrication routes that enable new devices architectures. Here, the assembly of gold nanorods (width ~15-30 nm, aspect ratio ~2-6, nanomolar aqueous dispersion) onto sub-100 nm polymer derived surface patterns (PDSP) is examined to determine the conditions necessary for selective absorption and the impact of commensurate length scales (i.e. confinement regime) on the ordering of the Au NRs. Using a site-specific functionalization chemistry to tune the surface property of the Au NRs, CTAB-free polyethylene glycol (PEG) and PEG- mercaptopropane sulfonate (MS) functionalized Au NRs have been created. At the appropriate pH, MS-AuNRs selectively interact via acid-base or electrostatics with cationic surfaces, such as poly2-vinyl pyridine (P2VP). In contrast, PEG-Au NRs preferentially absorb to hydrophobic surfaces, such as polystyrene (PS), analogous to protein adsorption on hydrophobic interface. This preferential interaction enables selective Au NRs absorption and thus replication of the underlying PS-P2VP pattern created by PDSP down to least 50 nm line widths. In contrast to prior studies on spherical nanoparticles, the NRs organization and orientation strongly depend on both size and pitch of the pattern, and the size and architecture (aspect ratio) of the rods. Large scale organization of such patterns provide novel anisotropic optical properties arising from hybridized plasmon modes associated with the engineered coupling of the AuNR plasmon resonances.

COLL 96

Magnetic assembly of nonmagnetic particles into photonic crystal structures

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We report the rapid formation of photonic crystal structures by assembly of uniform nonmagnetic colloidal particles in ferrofluids using external magnetic fields. Magnetic manipulation of nonmagnetic particles with size down to a few hundred nanometers has been difficult due to their weak magnetic dipole moment. By taking advantage of the superior stability of highly surface-charged magnetite nanocrystal-based ferrofluids, we have been able to successfully assemble 185 nm nonmagnetic polymer beads into photonic crystal structures, from 1D chains to 3D assemblies as determined by the interplay of magnetic dipole force and packing force. In a strong magnetic field with large field gradient, 3D photonic crystals with high reflectance (83%) in the visible range can be rapidly produced within several minutes, making this general strategy promising for fast creation of large-area photonic crystals using nonmagnetic particles as building blocks。

COLL 97

Phase behaviour and lubricating properties of fatty acids/diamine mixtures

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Water based lubricants are widely used in metal forming processes due to their good cooling and lubrication capabilities. Mixtures of diamines and fatty acids in water are some of the main ingredients of such lubricants. The goal of our work is to correlate the physico-chemical properties of fatty acids/diamine mixtures to their lubricating behaviour. Herein, the phase behaviour of these mixtures is investigated for different compositions. We propose that the observed succession of phases (micellar-hexagonal-lamellar) results from the evolution of the coupling between the amine groups and the fatty acids polar heads. The different phases were observed and studied using polarized light microscopy, Small Angle X-ray and Neutrons Scattering (SAXS and SANS) and Freeze-Fracture Transmission Electron Microscopy (FF-TEM). The investigation of the lubricating properties of

these different phases was conducted using an original experimental set up and shows that the lowest friction coefficients are obtained with the lamellar structure.

COLL 98

Marangoni flow-induced water droplet arrays as novel templates for fabricating polymeric micro/nano structures

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Ordered water droplet arrays induced by Marangoni-flow were utilized to fabricate polymer structures as an alternative to photo-lithography based approaches. During the formation of the water droplet arrays by Marangoni-flow, the arrangement of water droplet arrays can be tuned by varying the substrate wettability, humidity, rate of airflow and the thickness of the spread ethanol layer. The droplet size can also be independent tuned by further condensation or evaporation of formed water droplets, leading to porous polymer films with both close- and non-close-packed arrays of pores. The Marangoni-flow induced water droplet arrays, like the droplets resulted from the “breath figures”, could be an attractive and cost-effective alternative for creating nano/micro-scaled features that are commonly adopted for patterning applications.

COLL 99

Dynamic wetting and adhesion at hydrophobic surfaces

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A conducting droplet of an aqueous salt solution or an ionic liquid, in contact with air or immersed in an immiscible liquid, will electrowet a smooth, hydrophobic , insulator-coated electrode when a potential is applied. The advancing liquid contact angle decreases below the value at zero voltage as the potential is either increased or decreased. The electrowetting curves (contact angle versus voltage) are symmetric with respect to zero voltage and follow the Young-Lippmann equation below saturation. The reversibility is excellent and contact angle hysteresis is minimal. For a partially hydrophobized metal oxidesurface such as titania, the advancing water contact angle is a maximum at the point of zero charge, decreasing symmetrically on either side in a Lippman-like manner. In both of these examples of “electrowetting”, the increase in wettability of the solid surface arises from a reduction in the interfacial tension of the solid-liquid interface, γ_{SL}. During spreading the dependence of dynamic contact angle on wetting velocity can be predicted by the molecular kinetic theory (MKT) for large contact angles and by a hydrodynamic approach for small contact angles. There is a strong connection between liquid structure, work of adhesion, surface friction and molecular size. Liquid structure can be determined through X-Ray reflectivity studies. Surface heterogeneity has a strong influence on dynamic wetting behaviour- it appears that pinning of the three phase contact line can play an important role This dynamic wetting behaviour, irrespective of whether it is spontaneous [e.g. a droplet spreading during partial wetting] or forced [e.g. during electrowetting, or when a plate is immersed in a liquid] has significant ramifications for control of micro and nanofluidic flow in open channels as well as closed capillaries. We show that surface friction and slip length are closely connected.

COLL 100

WITHDRAWN

COLL 101

Influence of nanoscale geometric roughness on wetting behavior

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We describe our recent efforts aimed towards obtaining a better understanding of the effect of surface roughness on wetting behavior through the use of molecular simulation. Specifically, we examine the effect of nanoscale surface roughness (substrates with hills and valleys that have heights and widths in the 1-25 nm range) on wetting behavior. We work with two model fluids: Lennard-Jonesium and SPCE water. We focus on the evolution of the contact angle with variation of the amplitude and length scale of geometric heterogeneities as well as the strength of the substrate-fluid interaction. We probe a range of wetting behaviors that span from the Cassie regime, wherein liquid droplets sit atop asperities, to the Wenzel regime, wherein liquid droplets penetrate the contour, to the Inverse Cassie regime, wherein liquid droplets sit atop grooves filled with fluid.

COLL 102

Femtosecond laser irradiation to create controlled superhydrophobic surfaces

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Irradiation of metallic surfaces using ultra-short pulse laser results in dual scale structure. Inspiration from nature, micro/nano scale structures and surface chemistry are the most effective parameters in making superhydrophobic surfaces. According to our previous work [1], metallic surfaces are superhydrophilic immediately after micromachining by femtosecond laser. However, prolonged exposure to air turns surfaces superhydrophobic due to surface reactions and deposition of carbonaceous materials onto the surface. In this work, regular patterned structures are created in order to control the surface morphology and henceforth the level of superhydrophobicity. The reactions during and after laser irradiation are revealed by using different laser parameters and same roughness. In the range of lower laser power (below 500 mW) there is an optimum ratio of scanning speed and laser energy by which the irradiated surface has the best combination of surface chemistry and surface dual roughness that results into the maximum water repellency. [1]: Kietzig, A.M.; Hatzikiriakos, S.G., Englezos, P. *Langmuir* 2009, 25, 4821

COLL 103

Cassie to Wenzel transition for superhydrophobic films based on impedance measurements

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Applications of superhydrophobic films depend on their ability to remain in the Cassie state where discrete points along the surface support the aqueous phase and enable air entrapment at the film/water interface. For this reason, the design of superhydrophobic films should account not only for the basic compositional and geometrical requirements, but also for those factors that favor their stability and robustness. Here, we direct the Cassie-Wenzel transition for superhydrophobic polymethylene films to explore both the conditions and the mechanism in which the transition occurs. Using electrochemical impedance spectroscopy, we are able to unambiguously identify the characteristics of the Cassie and the Wenzel states and correlate the changes in impedance with that of the CA observed during transition. We also establish the kinetics of the transition as well as the ability of the system to reversibly recover the Cassie state after drying at ambient conditions.

COLL 104

Slippage of water at surfaces of varying wettability as a function of interfacial viscosity

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Classically, macro scale fluid mechanics has a no-slip (zero-velocity) boundary condition assuming the first layer of liquid molecules to be stationary relative to the solid. Recent work has challenged this condition at the micro/nano meter scale. The slip length is defined as the distance where the extrapolated flow velocity is zero. In the work presented, we relate the slip length b, to an effective interfacial viscosity between water and six different solid smooth surfaces of varying wettability. The nanorheology experiments are performed with an Atomic Force Microscope (AFM). The AFM tip endured lateral oscillations for concerted viscous lateral and structural normal force measurements as a function of tip-sample distance.

COLL 105

Molecular tilting in alkane film and its effect on friction

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The tribological property of hydrophobic n-alkane monolayer was studies by Atomic Force Microscopy/spectroscopy. We found that the alkane film has a higher co-efficient of friction (0.11) than octadecyltrichlorosilane (OTS) film (0.07), even though both of them are terminated with methyl group. In addition, alkane films in which alkane molecules tilt at a higher angle have a lower friction. At 0-28 nN range, the friction of the alkane film is a linear function of the loading force. The AFM tip (10 nm in size) partially penetrates the film when the loading force is between 28 -37 nN. In this force range, the film structure restores upon the removal of the loading force. In contrast, the tip shaves off the alkane molecule from when the loading force is above 37 nN.

COLL 106

Using PNIPAM nanogels in controlling the wettability properties of nano-probing devices

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Poly(N-isopropylacrylamide) containing polymer nanogels were synthesized by various methods, and subsequently used to modify the surfaces of polymer nano-probing devices. Nano-probing devices will contain two major elements; a tungsten wire core, and a fibrous polymer shell. Porous fibers made from PVDF were grafted with PNIPAM nanogels, with intent to aid in the retention and release of fluid from the probe and to alter their wetting properties by small fluctuations of temperature at or around physiological conditions. Our studies thus far have shown that small tungsten wires grafted with our particles exhibit changes in surface energy in aqueous environments above and below the LCST of the polymer system. Changes in surface properties of the wire were observed when droplets were placed on the modified wire. In parallel, wires dipped into a vessel containing water, showed dynamic changes in the formation of a meniscus.

COLL 107

Dewetting of stimuli-responsive hydrogel thin films

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The stimuli responsiveness arising from varying interactions between anions and imidazolium groups in copolymers of imidazolium-based acrylate monomers is also seen in homopolymers of 1-(11-acryloylundecyl)-3-methyl-imidazolium bromide. Besides nanoparticle formation of this hydrogel homopolymer, resulting from condensation with hexafluorophosphate and bis(2-ethyhexyl)sulfosuccinate anions in solution/suspension, thin films coated on quartz substrates from aqueous solution appear to dewet when exposed to anions such as hexafluorophosphate. This dewetting mechanism appears to result from structural relaxation after stimuli responsive anion exchange.

COLL 108

Dynamic bacterial interactions with surface-immobilized nanoparticles

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We have created a novel class of surfaces in which functionalized nanoparticles are embedded in a bio-compatible (nonadhesive) polymer brush. The nanoparticle diameter and brush height are chosen to be comparable, to set up a competition between steric repulsion of the brush surface against the bacteria and attractive interactions between the nanoparticles and the bacteria. In this investigation, the nanoparticles are cationic and the strength and range of their attractions with the bacterial surfaces is controlled with ionic strength. We demonstrate that the adhesive capture of flowing Staphylococcus aureus on these surfaces is both ionic strength and shear dependent. At modest shear rates, the ionic strength alters the presence of an adhesion threshold, a minimum density of nanoparticles needed for bacterial capture. High ionic strengths produce stronger electrostatic attractions and diminish this threshold effect, ultimately enabling bacteria to be immobilized by single nanoparticle-cell interactions. Stronger flow increases the threshold effect. We report parallel behavior between bacterial interactions with these nanoparticulate surfaces as has been previously reported by others for bacterial adhesion mediated by specific receptors.

COLL 109

Synthesis of silver nanoparticles supported on silicate platelets and their antibacterial activity

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A class of novel nanohybrids was synthesized by complexing silver nanoparticles (AgNPs) with silicate platelets and used for antimicrobial applications. We have tailored the synthesis of the nanohybrids consisting of AgNPs of different sizes supported on the exfoliated silicate platelets (NSP). Different AgNPs sizes from 3.8 nm to 35 nm diameter were tailored by adjusting the NSP weight ratios. The series of nanohybrids of AgNP/NSP were tested for antimicrobial inhibition. It was found that the efficacy was depended on the AgNP sizes, tested on the growth of dermal pathogens including *Escherichia coli* (*E. coli*), and *Staphylococcus aureus* (*S. aureus*). More important, the nanohybrid is effective for the silver-resistant *E. coli* (J53pMG101). Scanning electron microscope revealed that AgNP/NSP were adherent on the surface of individual bacteria. The hybridization of AgNPs on NSP surface allows the controls in AgNP sizes as well as prevention of AgNP adversary effect on cells.

COLL 110

Assessing the roles of ion-doping and water chemistry on the stability and antibacterial activity of ZnO nanoparticles using high-throughput screening approach

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The stability and bioavailability of nanoparticles is governed by their acquired interfacial properties when immersed in a particular aquatic media as well as the type of organism or cell under consideration. Zeta potential and aggregation state of dispersed ZnO nanoparticles was strongly influenced by iron doping; however, bacterial inactivation by ZnO nanoparticles was more significantly influenced by Zn^{2+} ions dissolution, bacterial cell type, and dissolved organic matter. Tannic acid decreased toxicity of ZnO to a much greater extent than humic, fulvic, and alginic acid because it complexed more Zn^{2+} ions, thereby reducing their bioavailability. These results underscore the complexities and challenges in assessing potential environmental impacts of nanotechnology. In one water body, a nanoparticle might be acutely toxic, but in another it might be inert. The high-throughput and combinatorial methods to be presented promise to rapidly expand the knowledge base needed for regulators to develop an appropriate risk assessment framework.

COLL 111

Taking advantage of the virus symmetries to probe cells

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Increasing number of groups are introducing virus particles as primary building blocks to generate ornate nanomaterials for a range of applications. The particles' exquisite symmetries and their potent genetic malleabilities confer certain advantages that are not available to other nanomaterials. Our current research focuses on genetically altering Tobacco Mosaic Virus (TMV) with ligands, and utilizing these viruses for cell studies ranging from cell adhesion to stem cell differentiation. Unlike previous display systems, the viruses are designed to present the ligands with consistent regularity (2130 copies of RGD with 2.5 nm spacing along the 300 nm TMV particle) which will affect a cluster of receptors. We examine how such patterns of ligands will recruit the corresponding integrin receptors, initiate adhesion, promote cell migration and differentiation. These results provide the foundation for exploiting the viruses directly for cell studies, and for examining the role of ligand patterns and geometries on cell responses.

COLL 112

Multifunctional mesoporous silica-based fluorescent sensor for chemical and biological probing

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A versatile solid-state fluorescent sensor has been designed by functionalizing large-pore mesoporous silica with 3-isocyanatopropyltriethoxysilane and dansylcadaverine. The functionalized mesoporous silica material was characterized by means of small-angle X-ray diffraction, nitrogen adsorption, transmission electron microscope, scanning electron microscope, ^{29}Si and ^{13}C solid-state nuclear magnetic resonance, confocal laser scanning microscope, and fluorescence spectrophotometer. This material exhibited highly selective Hg^{2+} sensing due to the fluorophore moiety grafted on its surface. Much interestingly, the Hg^{2+}-bound mesoporous material was able to be utilized in detecting various amino acids (especially highly sensitive to phenylalanine acid) in aqueous solution. More importantly, the dansylcadaverine-functionalized large-pore mesoporous material could be applied to fluorescent turn-on sensing of bovine serum albumin, demonstrating an all-round smart sensor in chemical and biological application.

COLL 113

Ultrastabilzation of magnetic nanostructure with multi-functionality: Cellular interactions.

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We have developed a general functionalization strategy using nitrodopamine to produce colloidal superparamagnetic nanostructures (MNS) with tailorable functional groups. These ligands can by synthesized in large scale, and utilized

for phase transfer of ultra-monodisperse iron oxide MNS synthesized in organic mediums. Additionally, as relaxivity (and T2 contrast) decreases exponentially with increased coating, these monolayer functionalized MNS offers improvements over traditional dextran and silica coatings, and can allow enhanced T2 MRI signals at lower dosages. Because the ligand can be tailored to accommodate a variety of functional groups, including carboxyls, thiols, nitrilotriacetate (NTA), azides, strepavidin and amines, a variety of biomolecule conjugation chemistry can be utilized to create application specific MNS. Tailoring of surface functional groups can produce colloidal stability in PBS, and other biologically relevant buffers. Resultant MNS are tested for changes in relaxivity, in vitro cell toxicity and cellular uptake. In addition to magnetites, this functionalization strategy can be applied towards a variety of other materials, including ferrites and metal-oxides.

COLL 114

Multivalency modulated nano-bio interactions: A case study for transferrin receptor targeted nanoparticles and cancer cells

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Transferrin receptor (TfR, CD71) has long been a therapeutic target due to its over-expression on many cancer cells. In this study, PRINT® nanoparticles were conjugated with TfR ligands for targeted drug delivery. Cylindrical poly(ethylene glycol)-based PRINT nanoparticles (diameter [d] = 200 nm, height [h] = 200 nm) conjugated with human transferrin (NP-hTf) or transferrin receptor antibody (NP-OKT9), showed highly specific TfR-mediated uptake by all human tumor cell lines tested, relative to negative controls (bovine transferrin (bTf) for hTf or IgG1 for OKT9). The targeting efficiency was dependent on particle concentration, ligand density, dosing time and cell surface receptor expression level. Interestingly, NP-OKT9 or NP-hTf showed little cytotoxicity on all solid tumor cell lines tested but were very toxic to Ramos B-cell lymphoma, whereas free OKT9 or hTf was not toxic. There was a strong correlation between TfR ligand density on particle surface and cell viability and particle uptake. NP-OKT9 and NP-hTf were internalized into acidic intracellular compartments but were not localized in EEA1 enriched early endosomes or lysosomes. Elevated caspase 3/7 activity indicates activation of apoptosis pathways upon particle treatment. Supplementation of iron suppressed the toxicity of NP-OKT9 but not NP-hTf, suggesting different mechanisms by which NP-hTf and NP-OKT9 exerts cytotoxicity on Ramos cells. Based on such an observation, the complex role of multivalency in nanoparticles is discussed. In addition, this observation also raises concerns for unanticipated off-target effects when one is designing targeted chemotherapy nano-delivery agents.

COLL 115

Role of counterions and hydrophobic spacers in amino acid based cationic assemblies and their transfection efficiency: A structure-activity investigation

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We have synthesized a series of cationic lipids having different counterions, that is either having $N^+H_3Cl^-$ or $N^+H_3TFA^-$ or NH_2 in the hydrophilic moiety and a different hydrophobic spacer length (i.e. 0, 3, 5, and 7 carbon molecules) between the hydrophilic head group and the hydrophobic tail. We have prepared cationic liposomes and characterized the size, phase transition temperature, and zeta potential of the liposomes. The transfection efficiency and toxicity of the liposomes have also been evaluated in COS-7 cell line either in the presence or absence of serum and compared with the Lipofectamine^{TM}2000. We found that both the counterions and the spacer length played a significant role in determining the liposome properties, toxicity, and the transfection efficiency. Moreover, the gene expression efficiency of counterions was as follows: $N^+H_3TFA^- > N^+H_3Cl^- > NH_2$. 1,5-Ditetradecyl-*N*-lysyl-*N*-trytyl-L-glutamate, having $N^+H_3TFA^-$ form in the hydrophilic head group, shows the highest transfection efficiency with low toxicity.

COLL 116

Guiding virus particles to integrin-displaying cells

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Virus (like) particles represent structurally regular and stable self-assembled nanoparticles that can be obtained with high yields within a short period of time. They can be used as scaffolds for the display of large numbers of cell- and tissue-targeting molecules or therapeutic agents in a well-defined manner. However, high selectivity in cell entry and tumor uptake has rarely been demonstrated. To overcome this obstacle, we coated a virus particle with PEG to

avoid unselective internalization and successfully functionalized the particle with an integrin ligand using Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC) to obtain a nanoparticle that selectively internalizes into several different cancer cell lines overexpressing RGD-binding integrin receptors. These coated nanoparticles therefore represent a convenient platform for the development of cancer therapeutics by providing the ability to serve as a highly selective drug carrier.

COLL 117

Ion sensing with colloidal nanoparticles

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Ion sensors based on colloidal nanoparticles (NPs), either as actively ion-sensing NPs or as nanoscale carrier systems for organic ion-sensing fluorescent chelators typically require a charged surface in order to be colloidally stable. We demonstrate that this surface charge can significantly impact on ion binding and thus affect the read-out. Sensor read-out is thus not determined by the bulk ion concentration, but by the local ion concentration in the nano-environment of the NP surface. We present a conclusive model corroborated by experimental data that reproduces the strong distance-dependence of the effect. This allows us to tune the response of analyte-sensitive fluorophores by modifying their distance to underlying nanoparticles.

COLL 118

Deformation and stability of lipid membranes in electric fields

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The challenges and recent advances in the theoretical modeling of lipid membrane dynamics in electric fields will be overviewed. Vesicle shapes and the stability and poration of lipid bilayers will be discussed in relation to the complex electromechanics of membranes: First, the lipid membrane is an insulating shell impermeable to ions. Second, it is essentially a two-dimensional incompressible-fluid sheet--under stress, lipid membranes store elastic energy in bending, while membranes made of cross-linked polymers are more likely to be stretched and sheared. Third, lipid membranes are extremely soft and they are easily bent by the thermal noise. I will show how the dynamical coupling of interface charging, membrane deformation, lipid density redistribution, and fluid motion gives rise to rich and sometimes surprising behavior of lipid membranes in electric fields.

This work is in collaboration with the groups of Dr. Rumiana Dimova (MPI-KG) and Prof. Michael Miksis (ESAM, Northwestern University)

COLL 119

Sorting of lipids and protein in bent membranes

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The sorting of lipids and proteins in cellular membrane sorting centers such as the trans-Golgi network, the plasma membrane, and the endocytic recycling compartment, lies at the heart of fundamental biological phenomena such as organelle homeostasis, membrane signaling, and trafficking. Our research is directed at understanding biophysical contributions to the sorting of membrane components, using experimental lipid model membranes, and analytical thermodynamic and membrane elasticity theory. We will present measurements of thermodynamically reversible membrane curvature sensing for severalperipherally binding membrane proteins, including toxins and membrane binding domains of endocytic accessory proteins, such as Epsin N-terminal homology domains, and N-BAR domains. Our recent research has furthermore shown that ideally diluted lipids are not significantly sorted in curvature gradients presented by a cylindrical membrane in contact with a large thermodynamic reservoir (a giant unilamellar vesicle). This finding is consistent with analytical theories as well as molecular dynamics simulations and indicates that lipid sorting needs to be amplified by cooperative interactions, as is indeed observed in vesicles composed of ternary lipid mixtures. Two regimes of cooperatively amplified curvature demixing are distinguished: a) the sorting in the weak segregation limit in compositions near a demixing phase boundary and b) the sorting in the strong segregation limit, deep in the coexistence region. We will describe both regimes by means of thermodynamic models and also discuss dynamic aspects of curvature sorting.

COLL 120

Interfacial modulation of mechanical-chemical coupling in membranes

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Mechanical-chemical coupling in biological membranes is not a passive consequence of membrane elasticity and its compositional diversity. Rather it is an active means by which membrane functionality (e.g., for signaling and

trafficking) is spatially organized. The causality of this coupling is bidirectional: local mechanical deformations, such as caused by extracellular physical forces, induce sorting of molecules and domains in cellular membranes. Conversely, chemical transformation of membrane molecules (e.g., by enzymatic chemistry) or changes in membrane composition prompt domain reorganizations and shape transitions in cellular membranes. In view of the emerging notion that dynamic organization of membrane domains might be the organizing principle in cellular membranes, this mechanochemical coupling assumes special - evolutionary, developmental, and functional -significance. This talk will highlight examples recapitulating such mechanochemical coupling, including those induced by interfacial physical forces and enzymatic chemistry, using in vitro model membrane configurations developed in our laboratory.

COLL 121

Tethered membrane patches and GUVs as tools in membrane biophysics

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DNA-lipid conjugates have been used to tether lipid bilayer patches and giant unilamellar vesicles (GUVs) either to fixed anti-sense DNA sequences covalently attached to a support or to the anti-sense DNA sequence displayed on a fluid supported bilayer [1]. In the first case, the tethers are fixed, while in the latter they can diffuse in the region between the two bilayer surfaces. In both cases, GUVs are initially tethered, then, depending on the number density of DNAs on the surface, the GUVs rupture to form patches. The first system produces stable patches or stably attached GUVs independent of lipid composition, while the second system requires specific lipid compositions to achieve stability.□ Both systems can be used as substrates for further manipulation using DNA-lipid fusion machinery we have developed [2]. This machinery can also be used to deliver integral membrane proteins to GUVs or patches. Because the patches or GUVs are held away from the underlying support at a distance determined by the DNA length, unfavorable interactions with the support are avoided, especially important when working with integral membrane proteins. When GUVs or patches are tethered to supported bilayers with mobile tethers of different lengths, interesting topological domains are formed where tethers of different length segregate. Advantages and disadvantages of this approach compared with tethered vesicles [3] will be discussed. [1] M. Chung, R. D. Lowe, Y.-H. M. Chan, P. V. Ganesan and S. G. Boxer, *J. Structural Biology,* **168**, 190-199 (2009). [2] Y.-H. M. Chan, B. van Lengerich and S. G. Boxer, *Biointerphases*, **3**, FA17-FA21 (2008); Y.-H. M. Chan, B. van Lengerich, S. G. Boxer, *PNAS*, **106**, 979-984 (2009). [3] Y.-H. M. Chan, P. Lenz and S. G. Boxer, *PNAS*, **104**, 18913-18918 (2007).

COLL 122

Dynamic morphologies of reconstituted actomyosin cortices

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The actin cortex is a thin shell that encases the cell, and exerts mechanical work to modulate cell shape during essential life processes, such as division and migration. It does so through the action of enzymes that continuously crosslink and contract actin, a network of semiflexible polymers coupled to the inner leaflet a phospholipid bilayer. A mechanical description of cortical contraction is elusive, as the activity of the cortex and membrane cannot be isolated from the numerous overlapping cellular processes. As a result, it is difficult to ascertain the precise balance between cortical and membrane tension that is responsible for changes in cell shape. To address this, we reconstituted a simple in vitro system, where the activity of the cortex/membrane composite can be isolated from cellular processes, and the contribution to overall shape can be understood piecewise. We find that the contraction of an in vitro actin cortex bound to the inner leaflet of an artificial lipid vesicle generates a variety of 'biomimetic' shapes, from local changes in vesicle curvature, reminiscent of cell blebbing that occurs during division, spreading, and apoptosis, to contraction of the diameter of the vesicle, similar to what happens during cell migration.

COLL 123

Kinetic control of phase domain shapes in phospholipid vesicles

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Phospholipids terminated with phosphatidyl choline headgroups, when cooled below their melting temperature, can reside in either a tilt or a ripple solid phase, manifest by different macroscopic shapes to the phase domains. Sometimes these are stripes, sometimes blobs, sometimes hexagons. The types of phases observed can be composition dependent, in two component systems still producing solid-liquid transitions; however, there is also a substantial influence of thermal history on the domains observed. Fast cooling typically produces hexagonal phase domains while slow cooling produces stripes. This talk explores this behavior and presents additional observations concerning combined thermal histories. The talk will also address and how ultimate phase shapes relate to the

nanoscale membrane morphology and possible phase diagrams, including metastable regions.

COLL 124

Orientation of lipid domains in giant vesicles by electric field

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We report on the orientation of lipid domains in giant vesicles using an electric field. The giant vesicles were composed of a phosphocholine matrix lipid and a synthetic lipid functionalized with an iminodiacetic acid (IDA) headgroup. Upon addition of Cu(II) the membrane surface provides strong affinity sites for histidine-tagged proteins. By tailoring the IDA lipids to yield high transition temperatures (Tg) we created phase separated structures in giant lipid vesicles. The gel phase IDA-lipid typically formed single domains that exhibited strong, selective affinity for his-tagged proteins. Using an electric field we found that these protein-membrane assemblies represent a polar structure that could be rapidly oriented in the field. We discuss developments of the capture, orientation, and subsequent deformation of the giant vesicle to form lipid nanotubular projections from protein-induced membrane deformation. These findings could be used to form and control nanofluidic networks using a combination of self and active assembly.

COLL 125

Novel bimetallic nanocrystals and their use as electrocatalysts for fuel cell applications

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Development of an efficient and cost-effective catalyst having superior activity and stability for oxygen reduction, the rate-determining step in low-temperature fuel cells, has been identified as the most imperative challenge. Recently, we have developed a new system by growing dendritic Pt arms with large surface areas and highly active facets on nanocrystals of another metal such as Pd with controlled sizes and shapes. This novel bimetallic system offers a number of attractive features over the conventional catalysts based on Pt/C. Even without optimization in terms of composition and morphology, this novel Pd-Pt bimetallic

catalyst was shown to exhibit mass-specific catalytic activity of almost three times greater than the state-of-the-art commercial Pt/C electrocatalysts, as well as enhanced stability. In this talk, I will discuss this new synthetic method including the nucleation and growth mechanisms, and their potential extensions to different metal systems.

COLL 126

Shape and composition controlled electrocatalysts of alloyed nanoparticles

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Shape-controlled and nanostructured metal alloy has been the subject of active research as highly active catalysts in fuel cell, battery, and other chemical conversion systems. Since each crystallographic plane provides different surface atomic and electronic structures, the morphology of the catalyst can affect the activities greatly. Among the various methods, solution phase synthesis has the unique advantage in the control of the size and shape of metal alloy nanoparticles. One major issue of the synthetic methods is the reaction conditions used in one protocol for controlling the shape and size of a material usually have to be changed dramatically when a different particle or shape is desirable. In this presentation, I will show that by carefully controlling the growth kinetics, tailored morphology of the metal alloy nanocrystals can be readily generated. The facet-dependent electrocatalytic properties of several Pt alloy catalysts will be demonstrated.

COLL 127

Theoretical study of electrochemical processes on novel platinum group metal catalysts

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Platinum group metal catalysts with higher mass activity and better stability are an essential ingredient for necessary improvements in fuel efficiency and performance. Progress in the design of superior catalysts is critically dependent on obtaining a much better theoretical understanding of elementary electrochemical processes at the solid surface. We have, therefore, undertaken a

comprehensive and systematic computational study of the structure, reactivity and stability of different materials based on platinum group metals such as Pt-Ni alloys and Pt nanotubes. The effect of structure and composition of these catalysts on the adsorption of O and OH species is explored using the plane wave, pseudopotential implementation of DFT. We have in addition investigated the stability of these materials in an aqueous environment by determining their most stable state as a function of pH and potential as represented in Pourbaix diagrams.

COLL 128

Graphene-supported PtAu alloy nanoparticles with enhanced activity for formic acid oxidation in direct formic acid fuel cells

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Graphene-supported Pt and PtAu alloy nanoparticles are prepared by ethylene glycol reduction method and characterized with XRD, SEM, HRTEM, XPS and EDX. X-ray diffraction reveals the face-centered cubic structure of Pt in the prepared materials. Electron microscopic images show the good dispersion of metallic nanoparticles on graphene sheets. Electrocatalytic performance of the materials is investigated by cyclic voltammetry and tested in a fuel cell. Formic acid oxidation activity of the PtAu/graphene is found to be nearly 12 times higher than that of Pt/graphene. Furthermore, the PtAu/graphene exhibited the overpotential 110 mV lower than that of Pt/graphene. Fuel cell tests also depict the good activity and stability of PtAu/graphene compared to Pt/graphene. The activity enhancement is attributed to the presence of Au underneath a thin Pt shell, where electron exchange between Au and Pt promotes the formation of active oxygen species on Pt, facilitating the removal of CO-like reaction intermediates.

COLL 129

Ternary PtSnRh–SnO_2 nanoclusters: Synthesis and electroactivity for ethanol oxidation

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Carbon supported ternary $Pt_{52}Sn_{(36-x)}Rh_{12}$–$Sn_xO_{2x}$ electrocatalysts with the average diameter of 2.8 $\pm$ 0.5 nm were synthesized using a Polyol process followed by thermal treatment. Several techniques including high resolution

transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X–ray absorption fine structure (XAFS) were used to identify the coexistence of homogeneously distributed Pt/Sn/Rh random alloy and non–alloyed SnO_2 throughout the catalyst. The $Pt_{52}Sn_{(36-x)}Rh_{12}$–$Sn_xO_{2x}$ catalyst showed superior long–term activity and stability towards ethanol oxidation than the commercial Pt catalyst. Our data of ternary Pt/Sn/Rh catalysts with different chemical compositions and crystalline structures also indicated that the superior performance of $Pt_{52}Sn_{(36-x)}Rh_{12}$–$Sn_xO_{2x}$ might result from the electronic effect of Pt/Sn/Rh random alloy.

COLL 130

Biomimetic morphology-control of Pt nanocatalyst

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We aimed to develop a biomimetic approach to synthesize noble metal NCs with desired shape. We successfully employed phage display technique as a mimic of the natural selection rule to obtain the peptide sequences which have specific binding ability to Pt micro wire. With Fmoc solid phase peptide synthesis (SPPS) technique, we synthesized the freestanding peptide with the selected sequence. Using the green chemistry, we were able to synthesize ultrasmall water-soluble Pt NCs with near-spherical shape and controllable sizes. In addition, we used the same peptide molecule to achieve the multipod Pt NCs with controllable pod lengths. The electrocatalytic characterization shows that the multipod Pt NCs display higher electrochemical specific area (ECSA) than commercial Pt black and can be potentially used cathode electro-catalyst for oxygen reduction reaction.

COLL 131

Electrocatalytic nanoparticle-modified carbon nanofoams

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The high surface area, through-connected networks of porosity and highly conductive framework make carbon nanofoams attractive materials for electrochemical power-source applications. These conductive carbon

nanoarchitectures can be readily synthesized and scaled in *x-y-z* by infiltrating commercially available low-density carbon fiber papers with phenolic resin. The resultant pore structure, ranging from nanometers to micrometers, can be tuned via adjustments in the synthesis. Carbon-fiber-supported polymer nanofoams can then be modified with thiophene "hooks" to anchor pre-formed metal nanoparticles (e.g., Pd, Au, Ag, Pt), resulting in electroactive carbon nanostructures containing less than a weight percent of metal colloid. The syntheses of these hybrid nanoarchitectures are described and the electroactivity of the ultraporous electrode structures for reactions of interest in fuel-cells, batteries and capacitors, will be evaluated.

COLL 132

Assessment of cytochrome c oxidase activity in reconstituted proteoliposomes

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We present a study on incorporating Cytochrome c Oxidase (CoC), an effective proton pump, by dialysis into liposomes reconstituted from selected lipids. Due to the initial small size of vesicles following dialysis, we subjected samples to a series of freeze-thaw cycles prior to extrusion through a 400-nm membrane to produce uniform proteoliposomes. In this talk, we will present results of protein activity measurements in the native state, and following freeze-thaw cycles and extrusion. Our preliminary results appear to indicate that, while a significant level of activity is lost during the processing steps, the protein may be active enough for facilitated ion transport across the membrane. We will also present results of extensive dynamic light scattering measurements to characterize and understand the growth of vesicles during processing.

COLL 133

Toluidine blue O electrodeposited on carbon nanotube modified interface for high-rate electrocatalysis of NADH oxidation

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Nanostructured interfaces were fabricated by electropolymerizing toluidine blue-O on a carbon nanotube (CNT) modified electrode with high-surface area, uniform, controllable properties, and excellent electrocatalytic activity towards NADH oxidation. The CNT were coated on a carbon support by casting a suspension of carboxylated CNT in DMF on planar and porous substrates. The resulting CNT-coated electrode possesses capacitance as high as 1.8×10^4 μF cm^{-2} at 0.85 mg cm^{-2} CNT loading, which is 1600-fold increase comparing to bare carbon electrode. Deposition of PTBO on CNT-modified electrode was successfully achieved by electropolymerization to create an NADH-oxidizing nanostructured interface. The interface demonstrates 1.8 mA cm^{-2} current density for NADH oxidation at 50 mV vs. Ag/AgCl in 10 mM NADH solution (pH 6) with 0.85 mg cm^{-2} CNT loading, a 250-fold increase compared to PTBO deposited on glassy carbon. This PTBO/CNT based interface is potentially applicable to high-performance bioconversion, bioenergy and biosensor systems where NADH-dependent dehydrogenases are involved.

COLL 134

Ion transfer properties of layer-by-layer films during contact electrification

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The work reports the interesting charging behaviors of layer-by-layer (LBL) films of strong polyelectrolytes and the role of ion transfer during contact electrification of these films. When they were brought into contact with another material (e.g., stainless steel), films with polycations as the outermost layer typically developed positive charge, while films with polyanions as the outermost layer developed negative charge. We exploited the system to create a naturally antistatic surface by fabricating LBL films terminated with a mosaic layer of polycations and polyanions using microcontact printing. The charging properties of such films were continuously tunable and full switchable. We also investigated the ion specific effects in the ion transfer process, and found that the propensity of the ion transfer properties followed a Hofmeister ion series: the most kosmotropic ions such as hydroxide and fluoride are more likely to transfer while the most chaotropic ions such as iodide and perchlorate barely transfer at all.

COLL 135

Photoelectrochemical investigations of hematite thin films

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Hematite (α-Fe_2O_3) has long been considered as a potential candidate for photo-catalytic water oxidαation because of a favorable valence band edge, reasonably low band gap, high stability and low cost. However, ony modest conversion efficiencies have been achieved, which has generally been attributed to the low diffusion length of minority carries in the semiconductor. While many methods of making nanostructured hematite have been examined to overcome the small diffusion length – by maximizing absorption of light and minimizing the distance over which holes must travel to be collected – efficiencies have remained low. We utilized atomic layer deposition (ALD) to deposit very thin films of hematite as model system to investigation the feasibility of using such geometric modifications to overcome short diffusion lengths. Due to the self-limiting mechanism of ALD, we were able to produce conformal, high aspect ratio hematite films with variable thicknesses. We will present results from studies of flat and nanostructured hematite electrodes deposited via ALD in contact with one electron outersphere redox couples. Results of this series of systematic investigations allowed us to determine the limiting processes of such thin film hematite electrodes will also be presented, along with strategies at overcoming these bottlenecks.

COLL 136

Design and reactivity evaluation of activated carbon-supported Ruthenium nanoparticles for aqueous phase hydrogenation of pyruvic acid

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In this work, we present a strategy for design of monodisperse Ruthenium nanoparticles immobilized on activated carbon (RuNPs/AC) and assess the reactivity of the catalyst for aqueous phase hydrogenation of pyruvic acid. The ruthenium nanopartilces (RuNPs) were synthesized by a thermal decomposition method using Triruthenium dodecacarbonyl as precursor, and n-dodecyl sulfide as the stabilizing ligand. Transmission electron microscopy (TEM) characterization showed that the particles have a narrow size distribution with an average diameter of about 5nm. RuNPs/AC were prepared by immobilizing the RuNPs on activated carbon using colloidal deposition and centrifugation. The

catalyst was calcined to remove the stabilizer from the particle surface and reduced by hydrogen. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) characterization of RuNPs/AC showed that the catalyst has a Ru content of 3.6 wt.%. We used the aqueous phase hydrogenation of pyruvic acid as a model reaction to evaluate the reactivity of RuNPs/AC. At a reaction temperature of 328K and hydrogen pressure of ~5 MPa with 0.10 g catalyst in 30 ml of substrate (20 mM pyruvic acid in water), more than 50% of the pyruvic acid was converted within 15 min, and more than 94% substrate conversion was observed in 120 min.

COLL 137

Extraction of free-lignin cellulose from red algae residues

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Cellulose is the main structural component of plants and algae, as well as one of the most abundant and renewable biomolecules with biocompatibility and biodegradable properties. It is a widely used polymer in the chemical, pharmaceutics and fuels industries, but its extraction from superior plants and use are limited by the interlinked biopolymer known as lignin. The red algae *Gellidium* is generally used for the production of agar, whose compounds of interest are located in the internal wall. During agar production, most of the components of the external wall remain and are rich in cellulose with the advantage that this type of algae does not have lignin contents hence cellulose is easier to extract. In this work we present results on the extraction of cellulose from residues of agar industries. The cellulose material was extracted from the residues matrix by neutral, acidic and basic treatments, followed by neutralization, drying and was then characterized by FT-IR and XRD. The best extraction treatment resulted to be the neutral procedure, due to a higher yield and major crystallinity shown by XRD diffractograms corresponding to microcrystalline cellulose. The remnant treatments led to more amorphous biopolymeric materials.

COLL 138

Intracellular trafficking of quantum-dot tagged receptors

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Quantum dot (QD) semiconductor nanoparticles exhibit intensely bright fluorescence and photostability that significantly exceed those of current fluorophores, making QDs suitable to be visualized as single particles for lengths of time heretofore not realized with conventional fluorophores. The use of QDs to study receptor signaling within live cells is one of great promise to the molecular and cellular signaling community; however, it is still unclear how cell signaling behavior may be affected by the presence of a QD tag. I will present the work that addresses the process by which cells traffic QD-tagged GPCR and tyrosine kinase receptors, from the extracellular plasma membrane surface to within endocytic vesicle compartments. Our results provide compelling evidence for the unique value of using QDs to access mechanisms of receptor-mediated signaling, at the molecular level and in real time.

COLL 139

Achieving cytosolic delivery of quantum dot nanoassemblies: From polymers to peptides

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We seek to take advantage of the unique spectral properties of semiconductor quantum dots (QDs) for use in cellular labeling and sensing applications. Their extreme brightness, photostability, ability to engage in FRET and multiplex assay configurations and their ability to serve as scaffolds for the construction of nanoassemblies make QDs a promising alternative to traditional organic fluorophores and fluorescent proteins. Paramount to their success in cellular labeling and sensing is the development of robust and non-cytotoxic methods for QD delivery to the cytosol. This talk will highlight a number of strategies for the biofunctionalization of QDs with polymers and peptides for cellular uptake and labeling of subcellular structures. Cellular delivery experiments utilizing these various schemes will be highlighted and the relative advantages and disadvantages of each approach will be discussed. Additionally, data on the long-term intracellular fate, stability and toxicity of QDs will be presented.

COLL 140

Peptide and protein responsive polymeric nanoassemblies

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@font-face { font-family: "Cambria"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 0.0001pt; font-size: 12pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } Nanoscopic vehicles that stably encapsulate guest molecules and release them in response to a specific trigger are of great interest due to implications in several therapeutic applications. For this purpose, we have synthesized highly stable polymeric nanogels, in which the kinetics of guest molecule release can be fine tuned by control over crosslinking density. The polymer nanogel precursor is based on an amphiphilic random copolymer, where introduction of variations such as molecular weight and percentages of hydrophilic vs. lipophilic monomers have allowed us to achieve control over its size. We have shown that the non-covalently encapsulated guest molecules can be released in response to a redox trigger, glutathione (GSH). We have also shown that *in vitro* uptake and release of the guest molecules from these nanogels depend on the crosslinking density.

COLL 141

Effect of fullerene-tubulin binding on microtubule polymerization

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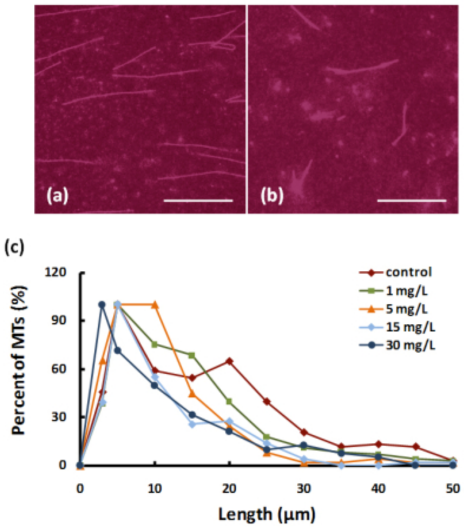
This study offers a molecular-level understanding on how nanoparticles may impact the assembly of cytoskeleton proteins, a topic of fundamental importance for addressing cell response to engineered nanoparticles. The *in vitro* polymerisation of microtubules was inhibited in the presence of a fullerene derivative $C_{60}(OH)_{20}$ at a concentration of 5 mg/L or above.



This inhibition was attributed to the interactions between the nanoparticles and tubulin heterodimers, as well as the hydrogen bonding between the nanoparticles and the nucleotides both in the hydrolysis reaction and imbedded in the microtubule protofilaments. Our circular dichroism measurement revealed a tendency for the $C_{60}(OH)_{20}$ to induce secondary structural changes in the tubulin, and our GTP hydrolysis assay further demonstrated the inhibition of inorganic phosphate release likely due to the hydrogen bonding formed between the nanoparticle and GTP. More direct evidence of tubulin and microtubule binding with the nanoparticle was provided by isothermal titration calorimetry measurements.

COLL 142

Engineered nano- and micron-sized silica particle-macrophage interactions: Effect of particle size and surface iron impurities on reactive oxygen species and lipid peroxidation production

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Potential applications of engineered silica in nanobiotechnology have increased over the years, but toxicological and pro-inflammatory properties of silica are not well understood. In this study, we investigated the influence of size and surface iron impurities on silica-induced inflammation in human THP-1 macrophages under non-cytotoxic doses. Nano (50 nm) and micron-sized (2 μm) engineered silica particles were doped with iron and characterized. The 50 nm nanoparticles triggered superoxide, lipid peroxidation and cytokines (IL-1β and TNFα) production in the macrophage membrane more than the 2 μm particles at 1 μg/ml. All these products increased significantly in the presence of iron and decreased when treated with iron chelator, deferoxamine mesylate. Tricychodecan-9-yl-xanthate, a competitive inhibitor of phosphatidylcholine-specific phospholipase C (PC-PLC), inhibited silica-stimulated cytokines induction. This data suggests that the reaction of iron impurities at the particle/macrophage interface triggers hydrogen peroxide and lipid peroxidation production, leading to the activation of PC-PLC and cytokine production.

COLL 143

Effect of curvature on the adsorption behavior of human serum albumin to polystyrene

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Nanoparticles are becoming widely used in various applications and make their way into the blood stream. When these particles come in contact with blood, human serum proteins quickly adsorb to the surface. The protein film on the surface will influence cellular response to these particles. Therefore, it is of interest to understand how the curvature of nanoparticles affects the adsorption behavior of human serum proteins. The model system under consideration is serum albumin adsorption to polystyrene nanoparticles and films. Dual polarization interferometry and quartz crystal microgravimetry are used to measure the adsorption of human serum albumin to smooth polystyrene films. A solution depletion method using capillary electrophoresis is used to determine the amount of protein adsorption to the 67 nm and 113 nm diameter polystyrene nanoparticles. Fitting various adsorption models to preliminary adsorption isotherm data suggests the maximum surface coverage increases and protein adsorption affinity decreases with increasing surface curvature.

COLL 144

Synergistic bactericidal activity of Ag-TiO_2 hybrid nanoparticles in dark condition

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We evaluated bactericidal activities of hybrid Ag:TiO_2 nanoparticles comprising variations in TiO_2 crystalline phase and Ag content using high-throughput screening methods in both light and dark test conditions. Hybrid Ag:TiO_2 nanoparticles were prepared by wet-impregnation and UV photodeposition on both Degussa P25 and DuPont R902 TiO_2 nanoparticles. Hybrid Ag:TiO_2 nanoparticles formed on P25 and R902 was proportional to the initial TiO_2 particle size. For experiments conducted under the influence of visible/UV light, all hybrid Ag:TiO_2 exhibited stronger bactericidal activity than UV, UV/TiO_2 or UV/Ag systems. In particular, P25 based nanoparticles produced greater bacteria inactivation rates than R902 based nanoparticles. For experiments conducted in the dark, bactericidal activity of Ag:TiO_2 nanoparticles was greater than either bare TiO_2 or pure Ag nanoparticles, suggesting the hybrid material produced a synergistic antibacterial effect unrelated to photoactivity. These results and the apparent mechanisms of enhanced antibacterial activity by the hybrid Ag:TiO_2 nanoparticles will be discussed.

COLL 145

Seeing theranostic nano-carriers by freeze-fracture electron microscopy

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The potency of nano- and micro-particles, loaded with therapeutic and/or diagnostics is frequently depending upon their morphology adopted in biological relevant environments. Freeze-fracture transmission electron microscopy (ff-TEM) as a cryo-fixation, replica TEM method is a powerful technique to monitor self-assembling of lipid-, polymer-, as well as protein/peptide-based carriers encapsulating drug-, gene-, vaccine, antimicrobial- and imaging molecules [1]. At a 2 nm resolution limit we are able to study structural modifications of such carriers related to their pay load, application milieu, and during cell interaction. Using ff-TEM we studied the morphology of a wide variety of nano- and micro particles suitable as carriers for diagnostics as well as therapeutics including quantum dots (coupled to drug-loaded immunoliposomes) [2], gold nano-particles, superparamagnetic iron oxide nano-particles loaded in polymeric immunomicelles [3], micelles (spherical-, disc-, and worm-type micelles) [4,5], small unilamellar liposome [6], multilamellar liposome, niosomes, cationic liposome/DNA complexes, integrin-targeted lipopolyplexes [7], polymer-, lipid- or surfactant-stabilized gas bubbles [8], cochleate cylinder, depofoam particles, and drug crystals. Recently we explored liposome-, virosome-, and virus-based vaccines, including measles vaccine powders, by ff-TEM. Furthermore, we investigated structural modifications within bilayers such as domain-formation [1]

but also transformations to non-bilayer structures such as hexagonal and cubic phases. ***References*** [1] B. Papahadjopoulos-Sternberg, In: Liposomes Methods and Protocols, Humana Press, 606 (2), 22 (2010) 333. [2] K.C. Weng et al. Nano Lett., 8 (12) (2008) 2851. [3] R.M. Sawant et al. J. Nanopart Res published online: 08/03/2009. [4] V.P. Torchilin et al. PNAS 100 (4) (2003) 1972. [5] Y.T. Ko et al. J. Controlled Release, 133 (2) (2009) 132. [6] V. P. Torchilin et al. PNAS 100 (10) (2003) 603. [7] P.C. Bell, et al. Biochem. 46 (2007) 12930. [8] S. Sirsi et al. Soft Matter 5 (2009) 4835.

COLL 146

Reduction in initial attachment of *Pseudomonas aeruginosa*, *Pseudomonas putida* and *Escherichia coli* by rhamnolipids

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Microbial biofilm formation on surfaces leads to significant losses in terms of energy, equipment damage, product contamination, and medical infections. The potentials of rhamnolipids, a group of bio-surfactants, in preventing/reducing the attachment of three bacterial species: *Pseudomonas aeruginosa* PAO1, *Escherichia coli* and *Pseudomonas putida*, on two different surfaces, glass and an organosilane modified hydrophobic surface, were investigated. The initial bacterial attachment was monitored inside a slow flow chamber. On the hydrophilic glass surface, a reduction of greater than 90% in attachment of PAO1 was observed, while the reduction in attachment of *E. coli* and *P. putida* was about 50% in the presence of rhamnolipids. On the hydrophobic surface, while the attachment of PAO1 was decreased by ~ 95% in presence of 200 ppm rhamnolipids, attachment of *E. coli* and *P. putida* only dropped ~ 60%. The effects of rhamnolipids on the hydrophobicity of the bacterial cells were examined and correlated to the attachment behaviors.

COLL 147

Quantized photoswitchable molecular probe for the cell membrane lipid phosphatidylserine

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Phosphatidylserine lipid is a critical constituent of cell membranes and an imbalance in its expression level is an indicator for ailments like cancer and Alzheimer's disease. Yet a robust technology for detecting and measuring it *in vivo* and *in vitro* does not exist. The biosensor Lact-C2-Cysteine-NBD that consists of two NBD (nitrobenzodioxazole) molecules attached to proximal cysteine residues on the C2 domain of the protein lactadherin developed in this study is a powerful biocompatible protein fluorescent molecule that addresses this technological need. It has been shown that the red fluorescence (670 nm emission) of proximal NBD molecules in Lact-C2-Cysteine-NBD probe shifts to green fluorescence (540 nm emission) upon binding to phosphatidylserine in the outer membrane of model phosphatidylserine-phosphatidylcholine vesicles due to the proximal to distal movement of the NBD molecules. The red fluorescence is restored when the probe unbinds and migrates through the lipid bilayer when the NBD molecules are again proximal. The red to green fluorescence shift is observed again when the probe binds to phosphatidylserine in the inner membrane. This entire process could be monitored by spectrofluorimetry and fluorescence microscopy in model vesicles and normal and cancer prostate cells. The fluorescence shift is likely due to the coupling of the electronic energy levels of NBD molecules when they are proximal (red fluorescence) and decoupling of this interaction when they are distal. This proximal to distal movement of the NBD molecules is caused by the binding of Lact-C2-Cysteine-NBD to phosphatidylserine and it is both photoaccelarated and reversible. A complementary phosphatidylserine probe Lact-C2-Lysine-NBD in which the NBD molecules are attached to distal lysine residues close to the lipid- binding site has also been generated and characterized. This probe exhibits a distal to proximal movement of NBD molecules and a green to red fluorescence shift when it binds phosphatidylserine.

COLL 148

Mimicking nature: Controlled membrane fusion between vesicles by specific coiled-coil interactions

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Membrane fusion has an overarching influence in living organisms. Intracellular membrane fusion facilitates molecular trafficking within every cell of the organism during its entire lifetime, and virus-cell membrane fusion may signal the end of the organism's life. Considering its importance, surprisingly little is known about the molecular-level mechanism of membrane fusion. Due to the complexity of a living cell, observations often leave room for ambiguity in interpretation. Therefore artificial model systems composed of only a few components are being used to further our understanding of controlled fusion processes. Recently, our group has designed simple synthetic analogues of SNARE proteins for controlled

membrane fusion. The model system impart all of the key characteristics to membrane fusion that are observed in SNARE mediated fusion. The mechanism of the fusion process will be discussed as well as recent advances in the fusion of vesicles (LUVs with GUVs). Possible applications as microreactors are discussed.

COLL 149

Molecular control of transbilayer plasma membrane phospholipid asymmetry: Substrate specificity and protein-protein interactions of the aminophospholipid flippase

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Phospholipids in biological membranes are distributed nonrandomly across the bilayer, with the choline-containing phospholipids enriched in the outer, and the amine-containing phospholipids localized to the inner, monolayer. This distribution is generated and maintained by inwardly-directed phospholipid flippases, floppase proteins that pump lipids to the outer surface and scramblases that facilitate the bi-directional movement of lipids. The plasma membrane PS flippase demonstrates a high structural and stereochemical specificity for PS that is distinct from other PS binding proteins, such as protein kinase C, clotting factors, and the macrophage PS receptor, but is shared by candidate flippases from erythrocytes and some members of a new subfamily (P_4) of P-type ATPases. Recent evidence also indicates that the activity of P_4-ATPases is regulated by the CDC50 family of proteins. Using activity inhibiting antibodies, our studies have also revealed that flippase and scramblase activities in erythrocytes are related; which implies that these transports may interact.

COLL 150

Fresh evaluation of cochleate cylinder by freeze-fracture electron microscopy: From fusion intermediate to carrier of antibiotics

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Cochleate cylinders are tightly wrapped, micrometer-size tubes of concentric bilayers folded in a spiral configuration. They were discovered during Ca^{2+}-induced fusion of small unilamellar vesicles made of phosphatidylserine [1]. Now they are used as platform technology for antigen delivery for vaccination and for oral drug delivery. Here we report the formation of cochleate cylinder by treating PS-free lipid films with cationic antimicrobial peptides without the requirement for divalent cations. The lipid films employed are mimicking the lipid pattern of cytoplasmic membranes of Gram negative bacteria. The antimicrobial peptides chosen contain the oligo-acyl-lysyl (OAK) sequence $C_{12}K\text{-}7\alpha_8$. Due to their cationic nature they replace the divalent cations in the cochleate cylinder forming process. Furthermore, this new type of cochleate cylinder has been proven to encapsulate and transport traditional, essentially ineffective antibiotics such as erythromycin to resistant bacteria cells [2]. The double-function of OAK-based antimicrobial peptides in forming cochleate cylinder and promoting encapsulation and effective delivery of traditional antibiotics in/by these assemblies provides an interesting approach to overcome antibiotic resistance in bacteria. ***References*** [1] D. Papahadjopoulos et al, BBA 394 (1975) 483 [2] L. Livne et al, FASEB J., in press

COLL 151

Emergent structures in lipid membranes

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Over the past several decades, supported lipid bilayers have been used as model systems of cellular membranes, to investigate various membrane interactions, and as platforms for development of bio-sensors. Precise structural characterization by neutron and x-ray scattering offers a wealth of insight into membrane organization, self-assembly, and domain formation as well as how membranes respond to changes in their environment, e.g. temperature, protein binding, etc. In this talk, I will discuss some recent advances in our understanding of supported membranes, their use in biotechnology applications, and highlight the importance of scattering techniques. [Figure 1]

COLL 152

Light driven formation of adhesive emulsion drops to form lipid bilayers

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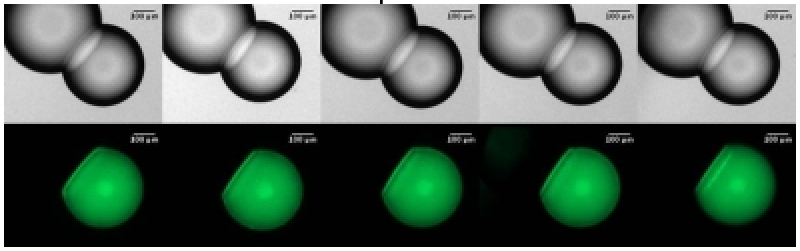
Biomimetic platforms for lipid bilayers are an attractive system to study the function of transmembrane proteins. We present an all optical, emulsion based, lipid bilayer platform to probe the dynamics of transmembrane proteins and peptides. The experimental approach builds on techniques developed in our laboratory [1] to manipulate water-in-oil emulsion droplets into adhesive contact. Our data indicate that labeled lipid molecules in one droplet remain confined to the same droplet after lipid bilayer formation as shown in the figure below. Lipid bilayers formed between droplet pairs are used as membrane platforms to insert transmembrane proteins. We show permeability characteristics of these bilayers and demonstrate the transport of molecules across these bilayer membranes.



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COLL 153

Cargo clustering promotes clathrin-coated pit initiation

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There is a repertoire of ways by which cells can dynamically remodel membranes. The major pathway for concentrative uptake of receptors and receptor-ligand complexes (cargo) into transport vesicles at the plasma membrane is clathrin-mediated endocytosis (CME). Although constitutively internalized cargos are known to accumulate into maturing and invaginating clathrin-coated pits (CCPs), whether and how cargo recruitment affects the initiation and maturation of CCPs is unclear. Previous studies have addressed these questions by analyzing the global effects of receptor overexpression on CME or CCP dynamics. Here, we exploit a refined approach using expression of a biotinylated TfnR (bTfnR) and controlling its local clustering using mono- or multivalent streptavidin. In contrast to overexpression studies, clustering of bTfnR increased the initiation density of CCPs. Combining live cell imaging by total internal reflection fluorescence microscopy and computational analyses of cargo-laden CCPs, we showed that bTfnR-containing CCPs mature more efficiently, though local clustering of bTfnR did not enhance CCP maturation. We further showed that CCPs containing bTfnR accumulated more adaptor proteins AP-2,

were larger, and exhibited significantly longer lifetimes than non-bTfnR containing CCPs. This demonstrates that variation in cargo loading is a key source of the differential dynamics of CCPs.

COLL 154

Graphene-based hybrid nanomaterials for energy storage applications

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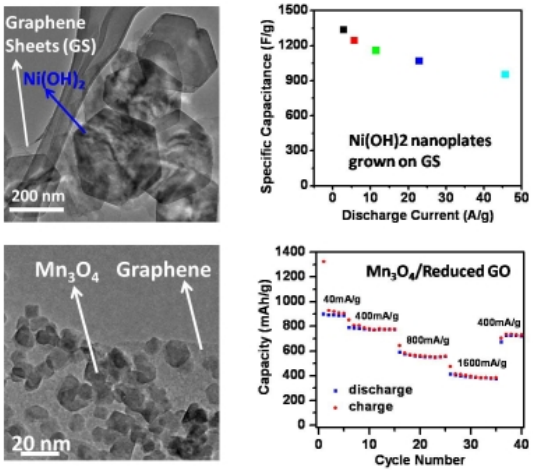
We have developed a two step solution phase method to selectively synthesize nanocrystals of oxide and hydroxide on graphene sheets. The morphology and size of the nanocrystals grown on graphene can be readily tuned by synthetic parameters. The hybrid nanomaterials showed high electrochemical performance for supercapacitors and lithium ion batteries, as a result of the intimate interactions between the active materials and the highly conducting graphene network, and the desired morphology and size of the nanocrysstals on graphene.



COLL 155

Nanostructured materials for high-performance Li-ion rechargeable batteries

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We synthesized amorphous and crystalline TiO_2 nanotube arrays of different phases for applications in high-performance Li-ion rechargeable batteries. TiO_2

nanotubes of different phases are compared for electrochemical properties and they all demonstrate significantly higher capacities than TiO_2 compact layer. The amorphous TiO_2 nanotubes with a length of 1.9 μm exhibit a capacity five times higher than that of TiO_2 compact layer even when the nanotube array is cycled at a current density 80 times higher than that for the compact layer. Furthermore, TiO_2 nanotubes of different dimensions are systematically studied for correlations between nanostructure dimensions and electrochemical performances. In another project, we employed atomic layer deposition (ALD) technique to deposit nanosized-thin Al_2O_3 coatings onto $LiMn_2O_4$ cathodes to improve the cycling performances. The ALD-coated $LiMn_2O_4$ shows enhanced cycleability than bare cathode or coated cathode via wet chemistry methods, as the ALD coating is dense, pinhole-free, highly conformal, and provides full coverage.

COLL 156

Sustainable routes toward Mn - spinel cathode materials

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The quest for reliable energy storage systems directed to sustainable use of electric energy (especially in tandem with solar or eolian energy generators) represents top priority in both academic and industrial settings. Among present energy storage technologies, the light weight, high energy density lithium ion batteries proved to be robust and reliable, while not reaching yet full maturity. Nowadays lithium-ion comes in a plethora of variants and the differences in the composition are mostly related to the cathode material. In this regard, spinel type lithium manganese oxides are the most promising cathode materials for lithium ion batteries because they are inexpensive, have low toxicity and could be easily prepared in comparison with other materials (lithium cobalt oxides and lithium iron orthophosphate). Routes to using safe, low cost and abundant Manganese precursors for Mn-spinel cathode production will be the focus of the presentation.

COLL 157

Nanostructured vanadium pentoxide film electrodes for highly efficient Li-ion batteries

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Nanostructured V_2O_5 films have been prepared by cathodic deposition from V_2O_5 and H_2O_2 followed by annealing at 500 °C in air. Related chemical reactions and films formation mechanisms were discussed. Crystallinity, surface morphology, microstructures and valence status of the films were investigated by means of XRD, SEM, XPS and AFM. Cathodic deposited nanostructured V_2O_5 films showed high initial discharge capacity of 402 mAh/g and 240 mAh/g retained after over 200 cycles when discharged at 1.3 C. The high energy density (900 Wh/kg at 1.3 C) and power density (28 kW/kg at 70 C), enhanced phase transitions as well as the good cyclic stability (well functioned over 200 cycles) could be ascribed to the unique nanostructure with higher surface area, shorter Li^+ ion diffusion path and improved mechanical integrity.

COLL 158

Investigation of hierarchical dual-size nanotextured surfaces

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The aim of this research is to develop hierarchical nanotextured surfaces which can greatly increase the performance of self-cleaning, antireflection, solar energy conversion, and catalytic systems. In this work, multilayer nanostructured surfaces composed of nanoparticles with dissimilar sizes and chemical compositions and the effect of these parameters on the overall chemical, mechanical, and optical properties of the surfaces were studied. Surfaces of nanoparticles such as SiO_2, Al_2O_3, and TiO_2, were chemically modified alternately with amine or epoxy groups. Degree of surface functionalization was measured by thermal gravimetric analysis. Multiple layers of chemically modified nanoparticles in an ethanol suspension containing fluorosilane additive were spin coated onto glass surfaces. Hydrophobicity and oleophobicity of each surface were investigated. Surface morphology was studied by scanning electron microscopy and spectroscopic methods. It was concluded that there is a strong relationship between physical properties of the surfaces and the order of nanoparticle deposition.

COLL 159

Enhancing photocurrent efficiency by cascade resonance energy transfer in panchromatic CdTe quantum dot multilayers

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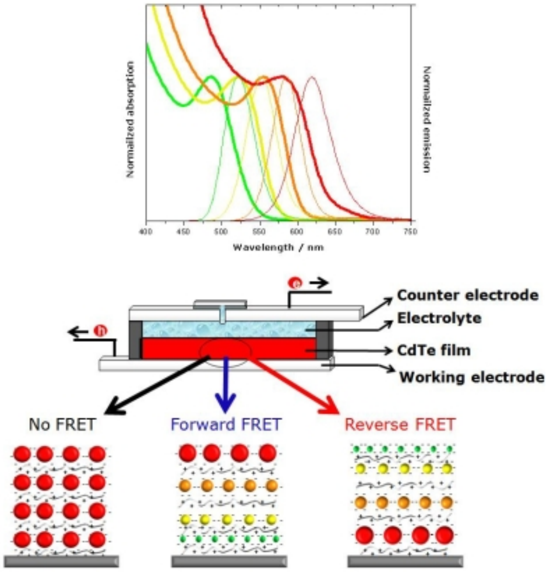
The present work demonstrates the impact of unidirectional cascade FRET[1] along an energy gradient on the performance of photoelectrochemical cells(PEC) thioglycolic acid capped CdTe quantum dots(QD) (TGA@CdTe) based.



Up:normalized absorption(thick lines)/emission(thin lines) spectra of different TGA@CdTe ($\lambda_{excitation}$420nm) in water. Down:PEC architecture and deposition order of CdTe QD. ForwardFRET and ReverseFRET refer to the energy transfer direction towards the CdTe/electrolyte interface and CdTe/ITO interface, respectively. Differently sized TGA@CdTe, namely 1.7(green), 2.5(yellow), 3.2(orange) and 3.5nm(red) were chosen to constitute an energy gradient from green and yellow to orange and red and to maximize the overlap integral between emission of excited state donor and absorption of ground state acceptor. In all cases four layers of TGA@CdTe were transferred onto ITO substrates by means of LbL deposition with poly(diallyldimethylammonium chloride) as interfacial linkers. Two photoelectrodes with FRET configuration, that is, “ForwardFRET” and “ReverseFRET” were constructed. Those refer to four TGA@CdTe layers with incrementally increasing and decreasing sizes respectively. A reference photoelectrode denoted as “NoFRET” consisting of four layers of TGA@CdTe with the largest available diameter was additionally constructed. The resulting samples, which revealed comparable absorptions, were probed in PEC. From the photocurrent measurement, the benefit of “ForwardFRET” is derived with enhanced photocurrent of around 32 % and 95% relative to “NoFRET” and “ReverseFRET” respectively. 1. Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

COLL 160

Fabrication and optical properties of multilayer thin films with upconversion nanocrystals

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Nanocrystals doped with Er^{3+} and $Yb^{3+}$are well known for exhibiting near infrared (NIR)-to-visible upconversion fluorescence, which is the emission of visible light when excited by NIR radiation. These nanocrystals are suitable for many applications, such as bioimaging, three-dimensional displays, solid-state lasers and photovoltaic devices. In this work, we have focused on incorporating Yb^{3+}, Er^{3+} doped β-$NaYF_4$ nanocrystals into multilayer thin films by utilizing layer-by-layer (LbL) assembly. The as-synthesized oleic-acid-capped $NaYF_4$ upconversion nanocrystals can be converted from hydrophobic nanocrystals to hydrophilic ones by extracting into a citric acid solution. The surface modified upconversion nanocrystals are uniformly deposited in the LbL thin films， and these thin films are characterized with atomic force microscopy and confocal upconversion fluorescence microscopy. In addition, the effect of the hydrophilic ligands on the upconversion properties of these nanocrystals is explored by characterizing the time evolution of upconversion emission following pulsed NIR excitation.

COLL 161

Developing volume memory devices based on functionalized nanoporous liquid spring

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In a hydrophobic zeolite, the infiltration and defiltration of water can be controlled by adjusting external pressure. The system behaves as a “liquid spring”, because the hysteresis of sorption isotherm is negligible. Addition of sodium chloride can lead to a significant increase in temperature sensitivity of infiltration pressure of a zeolite based liquid spring, which is beneficial to improving its output energy density. With the addition of sodium chloride, both infiltration and defiltration pressures increase, which should be attributed to the cation exchange. The temperature sensitivity of the system increases with the electrolyte concentration, also helps to reduce the already small extent of hysteresis of sorption isotherm,

beneficial to improving the output energy density. This effect should be related to the thermally aided cation exchange in nanopores. The working pressure is thermally controllable, therefore, volume memory devices can be developed based on this phenomenon.

COLL 162

Atomic layer deposition of TiO2 in enhancing the V2O5 xerogel film lithium ion intercalation capability

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V2O5 xerogel film was considered a favorable candidate for lithium ion intercalation application due to its lost cost and chemical stability. However, as-fabricated film without thermal annealing often exhibited severe capacity degradation after intial high capacities. Atomic layer deposition was used to attach atomic layers of TiO2 onto the film surface, to both enhance the mechanical integrity and reduce the active electrode dissolution during the repeated lithium ion intercalation/de-intercalation. It was found that atomic layer deposition of 5 to 20 layers all exhibited improved cyclic stability while capacity number indeed experienced decrease as compared with the inital capacity of the untreated V2O5. However, when the deposition was only 5 layers, the excellent balance between capacity number and cyclic stability was achieved. This could be due to the positive role of coated TiO2 atomic layer in suppressing the electrode dissolution and increasing electrode integrity.

COLL 163

Nonlinear sedimentation and electrophoresis of colloids

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The dynamics of a charged colloidal particle under gravitational (i.e. sedimentation) or electric (i.e. electrophoresis) fields are fundamental problems of relevance to several areas of science and engineering. The vast majority of previous works have focused on the “linear-response” limit, wherein the applied fields are sufficiently weak (in an appropriate dimensionless sense) to only slightly perturb the equilibrium diffuse screening cloud surrounding the charged colloid. In this regime, the sedimentation and electrophoresis problems are linked via the Onsager reciprocal relations. In this talk, we examine the motions of a charged spherical colloid under “strong” gravitational or electric fields, for which the diffuse cloud can be significantly distorted. We compute the sedimentation

and electrophoretic velocity over a range of field strengths and diffuse cloud thicknesses. In this nonlinear regime, subtle yet significant differences between motion under gravitational and electric fields are revealed.

COLL 164

Particle charging and charge screening in nonpolar dispersions with nonionic surfactants

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The electrostatic stabilization of colloidal dispersions is usually considered the domain of polar media only, but some surfactants are known to raise the conductivity of liquids with low electric permittivity and to mediate charge-stabilization of nonpolar dispersions. Here we report an example of the counterintuitive electrostatic effects of nonionic surfactants on colloidal particles in nonpolar solvents. PMMA particles in hexane solutions of sorbitan oleate (Span) surfactants exhibit a field-dependent electrophoretic mobility. In the zero field limit, we find large surface potentials whose decay with increasing surfactant concentration resembles the salt-induced screening in aqueous solutions. The amount of surface charge and screening ions in the nonpolar bulk is further characterized via ensemble measurements of the particles' pair interaction energy. In contrast to the behavior reported for systems with *ionic* surfactants, we observe particle charging and a screened Coulomb type interaction both above and below the surfactant's critical micelle concentration.

COLL 165

Effect of reverse micelle size and charging properties on the performance of electrophoretic imaging fluid

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Electrophoretic ink, used as imaging fluid, is the leading technology for commercially available reflective displays (e.g., e-book readers). Extending state-of-the-art for high fidelity color in reflective displays requires improved understanding and control of these colloidal systems. In these dispersions, reverse micelles in nonpolar media play key roles in the charging and stabilization of colorant colloidal particles. We investigate the effect of surfactant chemistry on reverse micelle size and charging properties using a surfactant

series synthesized with different polyamine heads, either mono- or di-substituted to a polyisobutylene tail. Reverse micelle size, zeta potential, and total charge in isoparaffin solutions are determined with dynamic light scattering, small-angle x-ray scattering, and transient current measurements. Colloidal particles are added to the solutions and electro-optical performance is evaluated with current measurements and video microscopy at various applied voltages in test devices.

COLL 166

Seismoelectric effect: A non-isochoric streaming current

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Propagation of ultrasound through a porous body saturated with liquid generates an electric response. This electroacoustic effect is called the “seismoelectric current”; the reverse process, when an electric field is the driving force, is called the “electroseismic current”. Seismoelectric currents can be measured with electroacoustic devices originally designed for characterizing liquid dispersions. Such electroacoustic device has to be first calibrated with a liquid dispersion and then used to characterize a porous body. We demonstrated such measurements of the seismoelectric current with electroacoustic devices in three different types of porous bodies. The first porous body was a deposit of solid submicron particles. We monitored the kinetics of the deposit formation on the surface of the electroacoustic probe. It allowed us to unambiguously confirm that the measured signal was generated by the deposit. We were also able to extract information about the porosity of the forming deposits. The second type of porous body was again a deposit, but instead of solid submicron particles, we used very large, porous glass spheres. According to classical theory, these glass particles are not supposed to generate any electroacoustic signal because of their large size. Nevertheless, we measured a strong signal, which was apparently associated with the pores of the particles. We were able to derive some conclusions about the dependence of the seismoelectric current on the pore size. The last tests were performed with cylindrical sandstone cores. These porous bodies have a very high hydrodynamic resistance that prevents measurement of the classical streaming current. We are able to measure a strong seismoelectric current that correlates with porosity of the cores. We present here theoretical interpretation of these experiments based on 70 years old theory by Frenkel, who described this effect in terms of streaming current of compressible liquid. .

COLL 167

Dynamics of plasticizer: di(propylene glycol) dibenzoate-d_{10} in poly(vinyl acetate)

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^{2}H solid-state NMR was used to probe the dynamics of the plasticizer di(propylene glycol) dibenzoate (DPGDB-d10) in mixtures with poly(vinyl acetate) (PVAc). ^{2}H NMR spectra were obtained from PVAc samples with different deuterated plasticizer contents at various temperatures. The experimental ^{2}H NMR line shapes were fitted using a set of simulated spectra obtained from the MXQET program. The simulation was based on the superposition of a two-site jump motion, 180° ring flips, and the isotropic motions.

COLL 168

Ions and charged macromolecules near the interface between two electrolyte solutions

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We study the microscopic equilibrium structure of ions and macromolecules near the liquid-liquid interface by means of classical density functional theory, and derive a self-consistent diffusion equation to study the slightly-out-of-equilibrium behaviour under an external electric field, generated by two capacitor plates parallel to the interface. We predict a charge separation near the interface due to different solvation energies of the constituents [1,2], and a tunable adsorption of particles. Under external electric fields, we find non-equilibrium behaviour, that can be attributed to widely separated time scales that are connected to phase transfer, build up of the screening layers, and bulk diffusion. By means of a simple equation of state, that extends well beyond the validity of conventional Debye-Hueckel theory, we obtain quantitative information about ion pairing in bulk, and discuss the consequences for the effective interactions between the macromolecules near the interface[3]. [1] JZ et al., J. Phys.: Condens. Matter 20 (2008) [2] W. Kung, F. J. Solis, and M Olvera de la Cruz, JCP 130, 044502 (2009) [3] JZ, and M. Olvera de la Cruz (submitted)

COLL 169

Facile synthesis of bimetallic nanostructures for catalytic production of commodity chemicals

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Nanoscale bimetallic particles are of great interest due to their importance in advanced technological applications. Synthetic procedures that produce gram-scale, well defined and monodisperse bimetallic nanoparticles with controlled size and shape is a continuing challenge in nanoscale science. We have developed new organic ligands that when used as stabilizers for metal nanoparticles, provide the ability to gain control of the particle size in one-step synthetic procedures. Monodisperse bimetallic nanoparticles were synthesized and characterized using spectroscopic, microscopic and x-ray techniques. We have further investigated the electrochemical quantized double-layer (QDL) charging differences of 1-4 nm metallic nanoparticles. Within this size range, the electronic properties transition from a bulk-like continuum of electronic states to molecule-like, discrete electronic orbital levels. We demonstrate the efficiency of the bimetallic nanoparticles as effective catalysts for conversion of organic acids into commodity chemicals.

COLL 170

Hydrogenation in microfluidic reactors using ruthenium nanoparticles

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We report on the fabrication, characterization and immobilization of catalytic ruthenium nanoparticles (Ru NPs) in microfluidic channels made from polydimethylsiloxane (PDMS). N-dodecyl sulfide (NDS) was used as the stabilizer for Ru NPs. The particles were characterized by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), which confirmed the composition and monodispersity of the Ru NPs. NDS-stabilized Ru NPs were immobilized on aminosilane-modified PDMS and glass surfaces containing hydroxyl groups, as confirmed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Ru NPs were then immobilized *in-situ* in sealed PDMS microfluidic reactors after similar surface modification. Catalyst loading in the microfluidic reactor was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The effectiveness of the *in-situ* immobilization of NPs in the microfluidic reactors was evaluated by hydrogenation of 6-bromo-1-hexene at room temperature and one atmospheric of hydrogen. An average one-pass conversion of 45% and selectivity of 100% were achieved in approximately

10 minutes of reaction time. Catalysts could be reused up to three times without significant loss of activity. The system was also used for the hydrogenation of bio-based pyruvic acid in parallel to a conventional batch system using Parr reactors. Results showed that the system could provide a tool for efficient and rapid evaluation of catalytic NPs and assessment of reaction mechanisms.

COLL 171

Nanostructured-materials design for thermoelectric applications

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Nanostructured materials have shown great promise for superior thermoelectric properties. Recently, thermoelectric properties were shown to be enhanced by nanostructuring and nanoparticle doping. Transport properties are determined by the band structure of the host material and the scattering of electrons with nanoparticles, phonons and impurities. Here we intend to do nanoparticle-scattering engineering in order to maximize the power factor, P. This is in effect an inverse problem, attempting to solve for the best nanoparticle scattering potential which maximizes P. The potential is characterized by the barrier height and the radius of the nanoparticle. We also allow a multilayered nanoparticle. We simply maximize the power factor with respect to the nanoparticle potential profile. A simple and fixed model is chosen for other scattering rates, as well as the dispersion relation for the bulk electrons. The results show under what conditions can the power factor be enhanced.

COLL 172

High-performance electrochemical capacitors enabled by metal-oxide-decorated carbon nanoarchitectures

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Carbon nanofoams and aerogels are attractive electrode architectures for high-power energy storage devices, such as electrochemical capacitors, due to such desirable properties as high specific surface area, electrical conductivity, and through-connected pore structure, but the energy densities of the resulting devices are limited because of their reliance on double-layer capacitance for charge storage. We have developed self–limiting deposition methods to incorporate conformal, nanoscale metal oxide (MnO_x, $LiMn_2O_4$, TiO_2, or FeO_x) coatings throughout the macroscopic thickness (70-300 µm) of the pre-formed fiber-paper-supported carbon nanofoam. Faradaic reactions (*i.e.*, pseudocapacitance) at the nanoscale metal oxide increase the mass-, area-, and volume-normalized capacitance (2- to 10-fold) of the carbon nanofoam without adversely affecting its characteristic high-power capability. The metal-oxide-carbon nanofoam architectures serve as device-ready electrodes in aqueous asymmetric electrochemical capacitors (ECs) that exhibit enhanced energy densities and comparable power densities relative to ECs composed of unmodified carbon nanofoam electrodes.

COLL 173

Active and selective platinum nanocatalysts for the aqueous phase hydrogenation of carbonyl bonds

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The chemoselective hydrogenation of carbonyl bonds is a key reaction utilized in various chemical industries during fine chemical synthesis. The capability to perform these reactions in the aqueous phase is particularly important for the processing of biorenewable feedstocks. Our research efforts take advantage of platinum nanocatalysts synthesized in the 1-10 nm size range and stabilized by poly(vinylpyrrolidone), or PVP. After characterization, these prepared nanocatalysts are employed in aqueous phase hydrogenations involving usaturated aldehydes and ketones. Through the measurement of turnover rates we have observed that these Pt nanocatalysts are highly active. In addition, the catalysts are selective for unsaturated alcohol formation with the aldehydes, but not with the ketones. We are currently examining parameters such as particle size, catalyst composition, and reaction conditions that lead to improved selectivity. By combining results together, we aim to enhance the knowledge of designing environmentally-friendly and efficient routes for manufacturing desired chemical commodities.

COLL 174

"Dirt-cheap" iron oxide electrode materials for lithium-ion batteries

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Emerging battery designs will utilize high-performance electrode materials that are inexpensive, non-toxic, and lightweight. In this vein, “dirt-cheap” iron oxide (e.g., rust-like) phases have been considered as insertion hosts for rechargeable lithium-ion batteries, but the raw mineral forms are generally impractical due to electrochemical instabilities. Cation-deficient maghemite, γ-Fe_2O_3, is a modestly better positive electrode material than other ferrite varieties because cation-deficiencies in the spinel lattice provide additional sites for reversible lithium-ion storage. We deliberately increase the vacancy concentration of maghemite by substituting a fraction of the Fe^{3+} content for high-valent transition metal cations (e.g., Mo^{6+}, V^{5+}). This physiochemical modification allows one to dramatically improve the lithium-ion storage capacity while maintaining a composition that is still predominantly iron-oxide. Aerogel and ambigel forms of these substituted ferrites are especially promising, because the highly porous three-dimensional architecture provides optimal electrode-electrolyte contact within a low-density framework.

COLL 175

Forces and friction between hair fibres and the effect of lipid structure

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The outer surface of hair consists of a palisade layer of lipids of different chemical structure. We consider the effect of the lipid structure on the interactions in both air and water between two such surfaces and the implications for lubrication. In addition we present novel measurements of the interactions betweeen two hair fibres and discuss the effect of directionality and angle.

COLL 176

Structural origins of the hydrophobic properties of the cosmetic substrate

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Keratin biological substrates like stratum corneum and hair are examples of natural hydrophobic surfaces. In both the membranes of the living cells that were at the origin of these evolved organs developed and structured forming an hydrophobic barrier against the more hydrophilic protein material. We will present a review of different experiments looking at the organization of these kind of surfaces done at our laboratories . For example, we have been interested in the friction and adhesion (tribology) properties of hair and upper skin cells (corneocytes) as well as the subtle alterations induced by water and other materials of cosmetic interest. We will present or on-going projects based on the combined use of Atomic Force Microscopy (AFM) and Electron Microscopy to elucidate the structure and role of specific covalently linked lipids at the surfaces. By Chemical Force Microscopy the chemical groups available at the substrate surface can be better explored. The hydrophobic interaction that we are lately able to measure in water is sustainably prone to disappear after weathering or other hair and skin aggressions. Cosmetic ingredients try to restore these interaction proposing innovative solutions for hair and skin protection and repair Combination of these versatile AFM techniques is highly interdisciplinary and helps us to advance towards the identification of the properties of the substrates and most importantly to understand the way a specific cosmetic treatment (new active or material) alter them.

COLL 177

Aqueous film rupture between hydrophobic particles and air bubbles measured by a novel surface force device

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Bubble-particle attachment plays a critical role in flotation. The aqueous film rupture, a critical step of bubble-particle attachment, depends largely on hydrophobicity. In this study, a novel surface force device was designed to determine the film rupture time. With the use of a solids state bimorph force sensor, the force applied to intervening aqueous film between an air bubble and a solid sphere can be finely controlled while the film rupture time recorded. Instantaneous film rupture was observed with hydrophobic surfaces while a repulsive force barrier was determined for solid surfaces of moderate hydrophobicity, leading to a finite rupture time which depends highly on surface hydrophobicity. The device also allows accurate determination of adhesion forces between air bubbles and solid spheres. Coupled with a digital video recording system, the advancing and receding contact angles were determined, thereby allowing accurate determination of capillary forces. The results show clearly the critical role of surface hydrophobicity in controlling the strength of bubble-particle attachment.

COLL 178

Building and characterization of polyelectrolyte multilayers assemblies on keratin fibers

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Polycation PDADMAC (+) / polyanion PSS (-) multilayer coatings were successfully transferred on keratin (hair) fibers. We have developed an original new method that uses negatively charged fluorescent microspheres as chemical probes to identify these polymer nanolayers directly onto the hair fibers, and by a combination of Dynamic Contact Angle and Fluorescent Microscopy. Water contact angles shows an inversion of the hydrophobic / hydrophilic character of the surface of the fibers after each treatment of the polycation and the polyanion respectively. Fluorescent microspheres in contact with the fibers treated with alternating PDADMAC and PSS deposits are adsorbed only at zones where the polycation is present. The obteined film is visualized and its thickness measured using AFM showing a monotonous increase from three to five layers. The concentration of salt in the solution of the polyelectrolyte has an important influence for the correct formation of these multilayer structure. In particular only at a salt concentration of 0.5 mol. l^{-1} this deposit is indeed organized in multilayers on hair. We observe that the growth of the thickness of layers with the ionic strength for hair fibers is lineal confirming the importance of the surface hydrophobic nature for this process. These differences of conformation of chains have a direct impact on the wettability of the layers and on their adsorption of charged microspheres. The screening of electrostatic charges brought by the salt is more likely facilitating an adsorption of polymer chains forming loops, whereas without salt, the chains adsorb in a flatter conformation (because of the electrostatic repulsions within the chain). The cosmetic properties of hair fibers in presence of water are also modified.. PDADMAC: poly [diallyldimethylammonium chloride], PSS: poly [sodium styrene sulfonate]

COLL 179

Spectroscopic and thermodynamic studies of the adsorption of surface-modified nanoparticles at the oil/water interface

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Self assembly of ligand - stabilized nanoparticles at the oil/ water interface has attracted a lot of attention in the past few years, due to the formation of complex interfacial structures with new collective properties. Our goal is to gain a better understanding of the underlying forces behind the particle self assembly at the oil/water interface. In our laboratory, vibrational sum frequency spectroscopy (VSFS) and surface tension measurements are employed to investigate the interfacial behavior of surface - modified nanoparticles at the CCl_4/water interface. VSFS is a surface specific spectroscopic technique that gives a valuable information on how particle self assembly is affected by pH, aqueous phase composition, particle surface modification and size. We find that particle adsorption is strongly influenced by particle hydrophobicity and size.

COLL 180

NaPSS-b-PS as a cosurfactant in emulsion polymerization

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In this study, we prepared sodium polystyrene sulfonate – b – polystyrene (NaPSS-b-PS), which exhibits surface-activity with NaPSS block as the hydrophilic moiety and PS block as the hydrophobic moiety. Using the stable free-radical polymerization technique, i.e., using benzoyl peroxide and 2, 2, 6, 6-tetramethyl- piperidinooxy (Tempo) as initiator in EG/H_2O(w/w=6/1) solution at 120C, we prepared NaPSS macroradical first, then polymerized with styrene to have the PS block. The NaPSS block has a Mw of 66700, and the PS block has a Mw of 29300, determined by the GPC. The critical micelle concentration in water of NaPSS-b-PS was determined to be 0.75 g/100mL. In the emulsion polymerization of styrene using the mixture of NaPSS-b-PS and SDS, although values of volume –average particle diameter (D_v) are larger, the polymerization rates are faster, comparing to those using mixtures of SDS and NaPSS. It is attributed to the lower capture rate of oligomer radicals into particles, based on the data of the degree of polymerization of product.

COLL 181

Metal-assisted and microwave-accelerated evaporative crystallization

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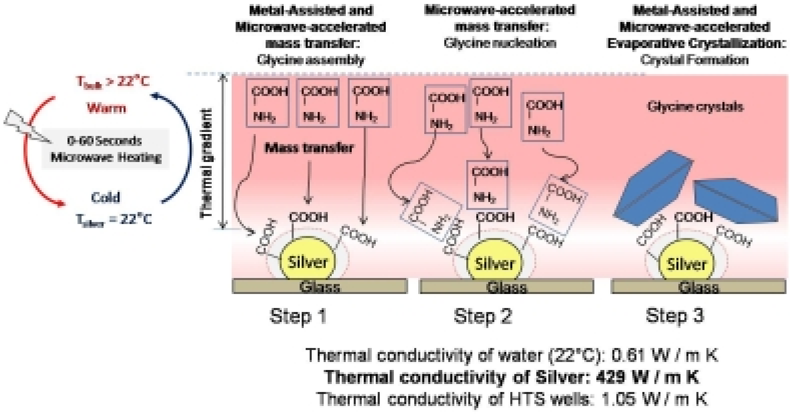
The understanding of molecular structures and interactions of proteins using crystallization to develop new drug treatments that target specific human diseases is an ongoing challenge to researchers in academia and in industry alike. Although many crystallization techniques exist, there is still need for one that affords better control over the crystallization process in a timely manner. We present a new approach to crystallization of small organic molecules, called Metal Assisted and Microwave Accelerated Evaporative Crystallization (MA-MAEC), which combines the use of metal nanostructures and low power heating to control and accelerate the crystallization process.



In the MA-MAEC technique, the use of metal nanostructures affords for the selective production of preferred polymorph and the low-power microwave heating affords for the significant reduction in the time (to seconds) of crystallization process. In this regard, we have tested our new technique with a model amino acid, which is glycine.

COLL 182

Rapid and sensitive colorimetric ELISA using silver nanoparticles, microwaves and split ring resonator structures

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We report a new approach to colorimetric Enzyme-Linked Immunosorbent Assay (ELISA) that reduces the total assay time to < 2 minutes and the lower-detection-limit (LDL) by 100-fold based on absorbance readout. The new approach combines the use of silver nanoparticles, microwaves and split ring resonators

(SRR). The proof-of-principle of the new approach to ELISA was demonstrated for the detection of a model protein (biotinylated-bovine serum albumin, b-BSA). The detection of b-BSA with bulk concentrations (1 uM to 1 pM) was carried out on commercially available 96-well high throughput screening (HTS) plates and silver nanoparticle-deposited SRR structures at room temperature and with microwave heating, respectively. While the room temperature bioassay took 70 minutes to complete, the identical bioassay took < 2 minutes to complete using the SRR structures (with microwave heating). A LDL of 0.01 nM for b-BSA (100-fold lower than room temperature ELISA) was observed using the SRR structures.

COLL 183

Gold nanoparticle based simple colorimetric and ultrasensitive dynamic light scattering assay for the selective detection of Pb(II) from paint, toy and environmental samples

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Pb (II) is a common environmental pollutant with high toxicity. According to the CDC, about 310,000 U.S. children ages 1 to 5 have high levels of lead in their blood and it is due to the exposure to lead from toys and other products. As a result, the development of ultrasensitive assays for the real-time detection of Pb(II) from toy and paint is very important for environmental controlling, clinical toxicology, and industrial processes. Driven by the need to detect trace amounts of Pb(II) from environmental samples, here we report, a label free, highly selective and ultra sensitive glutathione modified gold nanoparticle based dynamic light scattering (DLS) probe for Pb(II) recognition in 100 ppt level from aqueous solution, with excellent discrimination against other heavy metals. The sensitivity of our assay to detect Pb(II) level in water is about 2 orders of magnitude higher than the EPA standard limit. We have also demonstrated that our DLS assay is capable of predicting the amount of Pb(II) in paint, toys and water from MS river. A possible mechanism and operating principles of our DLS assay have been discussed. Ultimately, this nanotechnology driven assay could have <tt>enormous potential applications in </tt>rapid, on-site monitoring of Pb(II) from day to day sample.

COLL 184

Confining and controlling photoreactive molecules on surfaces

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Controlling how, where, and when molecules react remains a central goal of nanoscience. By manipulating the conformation, location, environment, and orientation of molecules with sub-nanometer precision, we can achieve direct control over the activity, reactivity, and selectivity of individual molecules. We have developed a system for monitoring and harnessing photochemical reactions and photocurrent/photoconductance generation of individual organic molecules with Ångstrom-scale spatial precision. Self- and directed assembly enable the *design* of the local environment around functional molecules. Photoreactive molecules may be deposited into defect sites singly, in pairs, or in groups within a well-defined self-assembled monolayer matrix. Photon scanning tunneling microscopy (PhotonSTM) enables measurements of molecules before, during, and after photoillumination and photoreaction.

COLL 185

Enhancement of hydrophobicity of ZSM-5 by surface silanization using alkyltrichlorosilane

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ZSM-5 zeolites were modified with different alkyltrichlorosilanes (octyltrichlorosilane, decyltrichlorosilane, dodecyltrichlorosilane and hexadecyltrichlorosilane) and characterized by Fourier transform infrared (FTIR), X- ray photoelectron spectroscopy (XPS), Thermal gravimetric analysis (TGA) and contact angle measurements (CA). The results showed that the surface grafting reaction took placed and the trichlorosilylated ZSM-5 zeolites surface processed superhydrophobic properties. The hydrophobicity increased with an increase in the alkyl chain length of trichlorosilane. Moreover, it was found that the hydrophobic properties of ZSM-5 particles could be tuned by changing the heating temperature before silanization. The hydrophobicity decreased with an increase in the temperature. The modified ZSM-5 zeolite may be used to enhance the separation performance of ZSM-5 filled silicone membrane for

removal of organics from aqueous solutions. **Keywords:** Surface modification; ZSM-5; alkyltrichlorosilane; superhydrophobicity

COLL 186

In situ synthesis of CdSe gradient shell nanocrystals: Their optical and structural characteristics

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Quantum dots have attracted considerable interest for use in various optoelectric applications because they have characteristics of size-tunable band gap with a narrow bandwidth, high photoluminescence efficiency. For desired optical properties of QDs, it is very important to reduce the presence of defects on their surfaces. Passivation of surface defects using larger band gap materials is the most effective way. Still mainly because of the lattice mismatch between two different materials, core and shell, creating high quality core-shell material with enhanced stability with high quantum yield is challenging. In this study, we created CdSe/gradient multi-shell structure. We then overcoated the core with CdS or $Cd_{(1-x)}Zn_xS_2$ to reduce the lattice mismatch through the one pot process. The properties of them were investigated by the various tools.

COLL 187

Smectic and columnar self-assembly of two-segment nanowires: Controlling assembly based on segment properties

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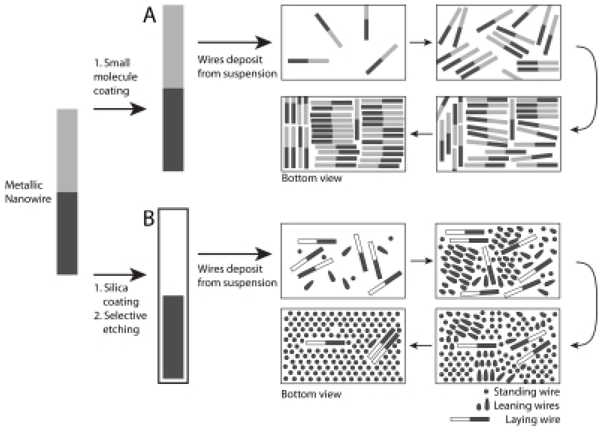
Improved understanding of assembly forces for nano- and microparticles will lead to enhanced control over resulting structures and bottom-up asssembly methods. Here, we examined the self-assembly of two-segment metallic nanowires (NWs), 290 nm by 2 to 8 μm, produced by electrodeposition within porous alumina membranes. Depending on the properties of the segments, the NWs displayed different assembly properties. As fully metallic NWs, with silica or small molecule coatings, were allowed to deposit from water suspension, smectic rows formed in which similar segments preferentially aligned due to a balancing of the electrostatic and van der Waals forces (Figure 1A). Alternately, nanowires that

contain a large density difference between the two halves spontaneously formed free-standing, columnar structures (Figure 1B).



COLL 188

Study of skin-surfactant interaction by skin impedance measurements

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The outmost layer of the skin, the stratum corneum (SC), has an ordered brick-motor (corneocyte-lipid) model structure and acts as the barrier between the body and the environment. It plays a very critical physiological role in regulating water loss/uptake through the skin and protects the body from a wide range of physical and chemical exogenous insults. When using surfactant-based cleansing products, skin damage and/or irritation are normally concerns since surfactants would reduce the skin barrier function, especially for sensitive skins like baby skin. It is generally accepted that reduction of skin barrier properties occurs only after surfactants have penetrated into the skin barrier. Therefore, to mitigate the harshness of surfactant-based cleansing products, penetration of surfactants has to be reduced. In this work, skin impedance measurements were conducted *in vitro* on porcine skin samples by using vertical Franz diffusion cells to investigate skin-surfactant interaction. Surfactant (SDS and SLES) solutions were studied based on their ability to perturb the skin impedance. The impact of various additives to the surfactant-based formulations was examined in detail. Factors such as the concentration and pH of the surfactant solution were also studied. It is observed that skin damage is dose-dependent and the skin impedance continues to decrease even beyond its CMC. Although not a dominant factor, pH plays an important role in regulating surfactant–skin interaction. This method can potentially be an easy, straightforward, and quick way to screen formulations in a high throughput approach.

COLL 189

Hydrodesulfurization properties of metal phosphide catalysts prepared from hypophosphite precursors

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Transition metal phosphide catalysts exhibit high activity for the hydrodesulfurization (HDS) of sulfur-containing compounds in petroleum. This research explored the synthesis and HDS properties of oxide-supported metal phosphide catalysts prepared using hypophosphite ($H_2PO_2^-$) as the phosphorus precursor. Nickel phosphide (Ni_2P), ruthenium phosphides (Ru_2P, RuP) and bimetallic phosphides of these metals ($Ru_xNi_{2-x}P$) were prepared on silica and alumina supports via temperature-programmed reduction of the precursors in flowing hydrogen. The metal phosphide catalysts had smaller particle sizes than the same metal phosphides prepared from phosphate (PO_4^{3-}) precursors. The effect of the phosphorus precursor on the dibenzothiophene HDS activities and selectivities of the catalysts will be discussed.

COLL 190

Synthesis and hydrodesulfurization properties of noble metal phosphide hydrodesulfurization catalysts

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Supported noble metal catalysts are highly active for deep hydrodesulfurization (HDS), but are sensitive to deactivation by sulfur. Noble metal phosphides (Ru_2P, RuP, Pd_3P, Rh_2P) supported on silica were prepared and their properties for dibenzothiophene and 4,6-dimethyldibenzothiophene hydrodesulfurization (HDS) were investigated. The HDS properties were compared with those of the reduced and sulfided noble metal catalysts having the same loading. A 5 wt% Rh_2P/SiO_2 catalyst was observed to be significantly more active than 5 wt% Rh/SiO_2 and sulfided Rh/SiO_2 catalysts. The product selectivities of the Rh_2P/SiO_2 and Rh/SiO_2 catalysts differed substantially, with the Rh phosphide catalyst more strongly favoring hydrogenated products. Based on hydrogen sulfide co-feeding experiments, the Rh_2P/SiO_2 catalyst was determined to be more sulfur tolerant than the Rh/SiO_2 catalyst and it incorporated less sulfur during HDS processing. Trends in HDS activity, selectivity and resistance to sulfur poisoning of the noble metal phosphide catalysts will be discussed.

COLL 191

Improved impregnation procedure for increasing available surface area and dispersion of active sites on sorbents and heterogeneous catalysts

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Current development of heterogeneous catalysts overwhelmingly focuses on the nature of materials used as opposed to the surface preparation method used to prepare the catalyst or the sorbent. In response to this trend, we propose a new preparation technique that increases dispersion of the active material upon a support. Through drop-wise addition of the desired material in solution, we can take advantage of surface tension forces at the molecular level to facilitate impregnation of the desired material. A further treatment follows using careful analysis by TGA and BET to aid further preparation of the material. Applications of this proposed impregnation technique have demonstrated significant improvements in the desired physical properties of the materials, in particular surface area and quantity of active sites. Furthermore, SEM analysis reveals a more regular surface morphology.

COLL 192

Modification of steel 316L and analysis of fibrinogen attachment

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Stainless steel 316L (SS316L) is a common alloy that has many material applications, such as medical implants. However, problems can arise due to bacteria and protein attachment to the surface, which can cause the device to fail. Therefore, modification of the SS316L surface is one possible solution to improve biocompatibility. The surface of SS316L was modified with both self-assembled monolayers (SAMs) of perfluorooctadecanoic acid (PFOA), octadecylphosphonic acid (ODPA) and (11-hydroxy)undecanephosphonic acid (OHPA), and a thin film of polypentafluorostyrene (PFS). The PFS was polymerized from a SAM. Monolayer formation and stability was determined by diffuse reflectance infrared fourier transform spectroscopy (DRIFT). Following surface modification, the samples were immersed in a solution of fluorescently tagged fibrinogen (0.2 mg/mL) for 2, 6, and 24 hours. The adhered fibrinogen was then analyzed using a Zeiss Axioskop. Five images were taken on each sample and the amount of protein attached was quantified using AxioVision software.

COLL 193

Preparation of Pt-Ru alloy electrocatalysts from hetero-binuclear complexes

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Platinum based alloys such as Pt-Ru, Pt-Fe, Pt-Co are promising electrocatalysts for methanol oxidation reaction (MOR). It is, however, difficult to prepare atomically mixed Pt alloy by conventional methods such as electrodeposition. Here, we propose a novel method to prepare atomically mixed Pt-Ru alloy from Pt-Ru hetero binuclear complex monolayer; adsorption of Pt-Ru complex on a Au(111) by immersing it into a Pt-Ru complex solution followed by heat treatment to remove organic ligands and form alloy. It is proved that Pt-Ru complex is adsorbed on Au(111) with partially ordered structure and dispersed Pt-Ru nanocomposites (3 nm in diameter, 0.3 nm in height) appeared after heat treatment at 300 ºC. These nanocomposites are mono atomic Pt-Ru alloy and the prepared electrode has high catalytic activity toward MOR. Effect of the repeating adsorption/decomposition cycle on the amount, shape and activity of the catalyst was also studied.

COLL 194

Hydrodynamic size variation and stability of triblock copolymer-modified Superparamagnetic Iron Oxide Nanoparticles: Implications for drug delivery

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Superparamagnetic Iron Oxide Nanoparticles [SPIONs] have promising potential in the field of drug delivery as they can be directed *in vivo* using external magnetic fields or conjugated molecular targeting agents. Monodisperse oleic acid-coated maghemite SPIONs[~6nm] were synthesized by thermal decomposition and characterized by TEM and XRD to determine size and structure. Samples of SPIONs were subsequently modified with 4 different commercially available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) tri-block copolymers, covering a wide range of molecular weights (5.75-14.6 kDa). The hydrodynamic radius and aggregation properties of each sample of SPIONS was studied by DLS. Magnetic properties of these nanoparticles were also studied. The partitioning behavior of a hydrophobic

carbocyanine dye model for hydrophobic drugs was studied by UV-VIS and fluorescence spectroscopy. The results of these studies inform the drug storage capacity, release characteristics and physiological stability of the SPIONs and will be advanced in *in-vitro* and *in vivo* drug release studies.

COLL 195

Non-electroneutral water has lower surface tension than neutral water

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Water dropped from a biased metal needle or under the electric field created by surrounding but non-contacting electrodes carries excess net charge. Accumulated charge within the Faraday cup by collecting water dropping from biased stainless steel needle has the same signal as the needle bias voltage. Surface tension of electrified water drops were measured by the hanging drop and drop weight methods. Electrified water has a lower surface tension than grounded water and becomes negative outside the ±7 kV range, when drops are deformed into Taylor cones, water jets and undergo coulombic explosion. Charge acquired by water drops under the electric field created by biased non-contacting metal is in agreement with a recent model for the electrification of insulators or isolated metals, based on charge transfer coupled to water evaporation, adsorption and desorption. These results are useful to develop new models and techniques for electrowetting, electrospray and electrospinning.

COLL 196

Humid atmosphere exchanges electric charge with glass surfaces

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DC voltage was applied to a couple of parallel, 6-mm wide, 8-cm apart Cu stripe electrodes laid on float glass (15 x 15 x 0.6 cm^3 sheet) surface and this was scanned with a 5-mm diameter Kelvin electrode placed 2 mm above. The measured surface potential showed a strong dependence on the ambient relative humidity. Under 10% RH, voltage is a linear function of electrode distance, as expected for a parallel plate capacitor. However, at 80% RH glass surface potential is negative throughout most of the inter-electrode area but the corresponding negative charge is dissipated at low humidity. Electric potential

profile and kinetics of potential variation under changing humidity confirm that charges are exchanged with the atmosphere, as expected considering a recent model for insulator electrostatic behavior, in which atmosphere is a charge reservoir for solids and liquids, mediated by water vapor adsorption and desorption.

COLL 197

Shell structures for enhanced thermal stability in Pt nanoparticle-based catalysts

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An approach based on a shell protective layer has been developed to enhance the stability of Pt nanoparticles in supported catalysts at high temperature. A model catalyst was first prepared by dispersing Pt nanoparticles on the surface of 120 nm silica beads, and then covered by a ~20 nm layer of mesoporous silica and etched to regain access to the metal. The structures were confirmed by transmission electron microscopy, and CO adsorption and 2-butene hydrogenation were used to evaluate the accessibility and catalytic activity of these catalysts. Without the silica protection, the Pt nanoparticles begin to aggregate from 600^{o}C, whereas the Pt nanoparticles protected by the mesoporous silica coating could resist sintering even at 800^{o}C.

COLL 198

Elasticity of *Staphylococcus epidermidis* biofilm grown under conditions of controlled stress and characterized by parallel plate rheometry

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The mechanical properties of the biofilm produced by *Staphylococcus epidermidis* RP62A (*S. epidermidis*) under physiologically relevant conditions were determined using parallel plate rheology. *S. epidermidis* is a biofilm-forming bacteria commonly found on medical implants, such as catheters and prosthetic heart valves, and may develop into a bloodstream infection. These biofilms are known to be viscoelastic fluids that can withstand transient changes in stress through reversible deformation (Shaw et al., 2004). Typically, non-standard rheological techniques have been used for mechanical property characterization because of the unusual environments in which biofilms thrive. We developed a method to grow healthy *S. epidermidis* biofilms directly onto the rheometer base, thereby eliminating the need to transplant and possibly damage the biofilm. Biofilms were grown on an enclosed rheometer peltier plate with the rheometer geometry (40 mm steel plate) rotating to create 0.10 Pa shear stress on the growing surface, a value within the range reported for the human circulatory system (Ross, 1998). Tryptic soy broth + 1-wt% D-Glucose media was pumped in a chemostat system at 0.6 ml/min and maintained at 37°C. The resulting biofilm was confirmed to be a monoculture of *S. epidermidis*. A series of oscillatory tests over a range of frequencies and rheometer plate gaps were conducted on the rheometer to determine the linear elastic and loss moduli. The effect of non-linear deformation on the biofilm mechanical properties is reported. Understanding the mechanical properties of this potentially life threatening biofilm may provide insight into its *in vivo* deformation, rupture, and dissemination.

COLL 199

Effect of amphiphilic media on covalent interaction between cisplatin and biomolecules

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Interaction of cisplatin and biomolecules is well known in the literature. According to the accepted mechanism the N7 nitrogen is the major target in DNA base guanine by cisplatin, a commonly used metal-based anticancer drug. In this study the covalent interaction between cisplatin with guanosine-5'-monophosphate and 9-methylguanine in micellar environment has been monitored. Different effect has been observed based on the charge on the surfactant headgroup utilized to prepare the micelles. ^{1}H NMR and UV-Vis spectroscopic techniques will be utilized to investigated the reactions between cisplatin and biomolecules. The size of the micelles will be determined using dynamic light scattering (DLS) technique.

COLL 200

Understanding globular protein structural rearrangement at oil-water interfaces

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The structure of protein at oil-water interfaces plays an important role in determining the stability and functionality of colloidal systems. However, the measurement of protein conformation at interfaces has been a challenge due to the high turbidity that arises from the colloidal droplets. In this study we have used synchrotron radiation circular dichroism to measure protein conformation *in situ* at interfaces in a colloidal system. We have shown that the adsorption to emulsion interfaces influences the conformation of globular proteins and the conformational rearrangement depends on the hydrophobicity of the oil phase. We have also investigated the geometric dimension of the globular protein adsorbed at a planar oil-water interface using the surface sensing dual polarisation interferometry technique, revealing unique information on the thickness and density of the protein interfacial layer. This work has provided further insight into the structural properties of proteins adsorbed at the oil-water interface and established new approaches for further study on protein interfacial behavior.

COLL 201

Selective catalytic isomerization of allyl alcohols using alkanethiolate-stabilized Pd nanoparticles: Effects of solvents and temperature

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This poster presents the study on isomerization of various allyl alcohols to the corresponding carbonyl compounds using Bunte salts-derived Pd nanoparticles. This study is extended upon our previous research on the isomerization of allyl alcohol to propanal. The selectivity of the catalytic isomerization of an allyl alcohol in the presence of second allyl acohol with different structure was investigated as well. Using NMR spectroscopy, the catalytic reactivity of Pd nanoparticle catalysts was examined for a two compound combination mixture which consisted of allyl alcohol, penten-3-ol, 3-methylbut-2-en-1-ol and/or but-2-en-1-ol. For the optimization of catalytic reactions of various allyl alcohols, the reaction conditions such as the type of solvents or the reaction temperature were controlled. Upon temperature increase, the rate of catalytic reactions generally became faster and produced the carbonyl compounds in high yields even for some of substituted allyl alcohols. Our results also demonstrated that the

solvents control the catalytic reaction pathway toward either isomerization or hydrogenation reactions. It appears that nonpolar solvents (e.g. benzene and chloroform) drive the reaction towards isomerization and polar protic solvent (e.g. methanol or water) drive the reaction towards hydrogenation. More understanding towards to the selectivity and reaction mechanisms of alkanethiolate-functionalized Pd nanoparticle catalysts will increase the future applications in organic synthesis and help to optimize the efficiency and selectivity of nanoparticle catalysts.

COLL 202

Synthesis of dendron-functionalized monodisperse gold nanoparticles

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Past and present utilization of metallic-cored nanoparticles in areas such as bio-labeling, receptor-mediated drug transport, and catalysis are strictly predicated upon the control of size and size distribution. In particular, gold nanoparticles are among the most widely explored due to its interesting optical and electronic properties as particle size decreases. Earlier methods have successfully produced gold nanoparticles with the average diameter between 1-2 nm with a high monodispersity. Nanoparticle-cored dendrimers (NCDs) represent the dendrimer materials with a nanoparticle core and well-defined dendritic wedges. Unlike dendrimers, the currently known NCDs do not have uniform molecular weight and densities. Our synthetic method is based on a strategy in which the synthesis of monolayer-protected nanoparticles is followed by adding dendrons on functionalized nanoparticles by a single coupling reaction. This allows us to build dendritic frameworks around a nanoparticle core, so that the size of nanoparticle core can remain same for NCDs after dendron functionalization. Here, we report a synthetic approach of generating monodispersed gold NCDs utilizing Au_{25} nanoparticles as a template. A thiol ligand with a reactive COOH functional group was introduced to the monolayer of the nanoparticles through the process of ligand exchange. The COOH functional groups allow the direct coupling of dendron wedges in a convergent method onto the surface of the gold nanoparticles while preventing any disruption to the gold core. This study represents the first availability of an effective synthetic method for highly monodisperse NCDs, which will allow us to further elucidate the relationship between primary structural elements in these nanostructures and their optical and/or electronic properties.

COLL 203

Preparation and surface functionalization of gold nanoisland arrays for interactions with Concanavalin A

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The research presented focuses on the preparation of glucose functionalized gold nanoisland arrays of varying size using self-assembly and heating methods. First, nanoparticle multilayer films were grown layer-by-layer (LbL) on glass slides by alternating exposures to functionalized gold nanoparticles and ionic polymers (linkers). Second, thermal evaporation of organic matters from nanocomposite films at 600 °C allowed the nanoparticles to coalescence and form nanoisland thin film arrays on the slide surface. The use of different sized particles resulted in nanoisland films with various domain size and density. The nanoisland arrays produced by this procedure displayed strong surface plasmon resonance bands in UV-vis spectra with a peak absorbance occurring at ~540 nm. The nanoisland films were then functionalized with an organic monolayer containing D-glucose. Interactions between glucose and ConA were used to investigate the optical sensing capabilities of the nanoisland films by exposing the glucose functionalized nanoisland films to a ConA solution and measuring resultant transmission surface plasmon resonance. The interactions between ConA and glucose resulted in a shift in intensity of the localized surface plasmon resonance. For example, in the nanoisland films prepared from 2 nm nanoparticles, there was a distinct change of ~1.5 nm in the SP band after exposure to ConA. Our analysis suggests the presence of carbohydrate-protein interactions occurring on the nanoisland surface and the attachment of a glucose monolayer to the nanoisland arrays.

COLL 204

Exploring the catalytic property of alkanethiolate-capped Pd nanoparticles with different core sizes and ligand density

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Recently, we have shown that Pd nanoparticles stabilized with alkanethiolate monolayers could catalyze the isomerization of allyl alcohol to propanal. When Pd nanoparticles were synthesized using sodium S-alkylthiosulfate (Bunte salts), the dissociation of alkylthiosulfate groups resulted in the formation of alkanethiolate ligands and sulfite moiety (SO_3^-) on the surface of Pd nanoparticles. The dissociation to alkanethiolate and the eventual elimination of

sulfite groups from the nanoparticle surface allowed both the sufficient monolayer coverage via the sulfur-palladium bond formation and the supplementary spacing between alkanethiolate ligands. The resulting lower density of organic monolayer surrounding Pd nanoparticles provided the increased catalytic activity as well as the higher selectivity toward isomerization of allyl alcohols over hydrogenation. In this study, the synthesis of Pd nanoparticle catalysts using Bunte salts is re-visited to explore the capability of controlling the core size and ligand density of these Pd nanoparticles. Furthermore, the catalytic activity of these Pd nanoparticles is investigated as well. These studies provide a better fundamental understanding on the role of monolayers surrounding Pd nanoparticles in selective catalysis.

COLL 205

Binding of dengue virus particles and dengue proteins onto solid surfaces

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The interaction between dengue virus particles (DENV), sedimentation hemagglutinin particles (SHA), dengue virus envelope protein (Eprot) and solid surfaces was investigated by means of ellipsometry and atomic force microscopy (AFM). The surfaces chosen are bare Si/SiO_2 wafers and Si/SiO_2 wafers covered with concanavalin A (ConA), jacalin (Jac), polystyrene (PS) or poly(styrene sulphonate) (PSS) films. Adsorption experiments at pH 7.2 and pH 3 onto all surfaces revealed that (i) adsorption of DENV particles took place only onto ConA under pH 7.2, due to specific recognition between glycans on DENV surface and ConA binding site and to electrostatic interaction between positively charged DENV surface and negatively charged ConA surface; (ii) DENV particles didn't attach to any of the surfaces at pH 3, confirming the presence of positive charges on DENV surface; (iii) SHA particles are positively charged at pH 7.2 and pH 3 because they adhered to negatively charged surfaces at pH 7.2 and repelled positively charged layers at pH 3 and (iv) SHA particles carry polar groups on the surface because they attached to silanol surfaces at pH 3 and avoided hydrophobic PS films at pH 3 and pH 7.2. The adsorption behavior of Eprot at pH 7.2 revealed affinity for ConA > Jac > PSS > PS ~ bare Si/SiO_2 layers. These findings indicate that selectivity of the Eprot adsorption is higher when it is on the virus surface than when it is free in solution. The correlation between surface energy values determined by means of contact angle measurements and DENV, SHA or Eprot adsorption behavior was used to understand the intermolecular forces at the interfaces. A direct correlation was not found because the contributions from surface energy were probably surpassed by specific contributions.

COLL 206

Specific ion effect on the colloidal stability of poly(ethylene glycol) decorated nanoparticles

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Poly(methyl methacrylate), PMMA, particles were synthesized by means of emulsion polymerization using poly(ethylene glycol) sorbitan monolaurate (Tween-20) as surfactant. The colloidal stability of PMMA/Tween-20 particles was investigated by means of turbidimetric measurements in the presence of NaF, NaCl, NaBr, NaSCN, KCl, $MgCl_2$ and $AlCl_3$. In agreement with Hofmeister anion series SCN^- was, among the four anions (F^-, Cl^-, Br^-, SCN^-) studied, the least effective in aggregating the colloidal particles. The effect of cations (Na^+, K^+, Mg^{2+}, Al^{3+}) on the dispersion instability was contrary to the original Hofmeister cation series. The colloidal behavior was associated with the interaction between Tween-20 located at the particle surface and the different anions with basis on surface tension measurements performed for Tween-20 solutions in the presence of the same ions. The area occupied by Tween-20 molecules at the liquid-air interface was the largest in the presence of the SCN^-, indicating large penetration of SCN^- ions into the Tween layer. Such penetration seems to cause the formation of a new charged surface, which favors stabilization due to electrostatic repulsion. Cations penetrated weakly in the Tween-20 monolayer at the liquid-air interface and the colloidal behavior observed for PMMA/Tween-20 particles might be due to complexation effects. However, SAXS data indicated that hydrolized Al^{3+} ions adsorbed strongly onto the hydrophilic outmost layer, explaining the highest colloidal stability in the presence of these cations.

COLL 207

Conjugation of ginsenoside Rg3 with gold nanoparticles

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Aims: Ginsenoside Rg3 was reported to have important biological activities. We demonstrate conjugation and quantification procedures of ginsenoside Rg3 to gold nanoparticles for future biological and medical applications. Materials & methods: Ginsenoside Rg3 was conjugated to spherical gold nanoparticles using a bifunctional heptaethylene glycol linker. The sulfhydryl group of heptaethylene

glycol was adsorbed onto gold nanoparticles, and carboxylic acid end of heptaethylene glycol was bonded through a hydroxyl group of Rg3 *via* ester bond formation. Results & Discussion: The conjugation of Rg3 was characterized with various spectroscopic techniques, high-resolution transmission electron microscopy, and using Rg3 monoclonal antibody. The Rg3- functionalized gold nanoparticles were 4.7 ± 1.0 nm in diameter with a surface charge of -4.12 ± 0.38 mV. The number of Rg3 molecules conjugated one nanoparticle was determined to be ~6 molecules by uing Rg3 monoclonal antibody. Conclusion: These results suggest that ginsenoside Rg3 is successfully conjugated to gold nanoparticles *via* heptaethylene glycol linker. The quantification was performed by using Rg3 monoclonal antibody without interference of gold's intrinsic color.

COLL 208

Self-assembly of the multi-segmented Se-Te-Se nanorods

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The side-by-side assembly of nanorods is an interesting phenomenon in nanoscience. Typically, this assembly is well understood by the energetic effect originated from the parallel interaction between nanorods and the entropic effect by minimizing the excluded volume of solvent during evaporation. The basic understanding of side-by-side assembly in nanorod system is further explored in the multi-segmented Se-Te-Se nanorod system. The multi-segmented nanorods shows complex assembly behaviors due to the structural complexity and the difference in chemical affinity between different segments. We report that the solvent effect, surfactant effect which affect the assembly of the multi-segmented nanorod system.

COLL 209

Fabrication of multifunctional nanostructures

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We propose a general process that allows convenient production of multifunctional colloidal particles by direct self-assembly of hydrophobic nanoparticles on host particles containing thiolated silica surfaces. These multifunctional particles will have applications in many areas, including catalysis, energy, labeling and detecting, drug delivery, and multiplexed bioassays. By starting with host particles containing a high density of surface thiol groups,

hydrophobic nanocrystals of various compositions and combinations can be directly assembled onto the host surface. The assemblies will be further overcoated with a layer of normal silica to stabilize the assemblies and render them highly dispersible in water. By forming another layer of mercapto-silica coat on the host particles, nanoparticles of different compositions and properties can be introduced onto the host particle surface in a layer-by-layer (LbL) manner. This self-assembly approach will provide the research community a highly versatile, configurable, scalable, and reproducible process to produce various multifunctional structures.

COLL 210

Adhesion force measurements of thin films using a JKR-type adhesion tester

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We have designed and developed a JKR-type (Johnson-Kendall-Roberts) adhesion tester to study adhesion at interfaces created by various organic materials. The instrument is set up on an inverted microscope, and consists of three major components: (1) a stepper motor that controls the position of the contact probe, (2) load cell to measure the force between the probe and the sample, and (3) a CCD camera to capture the image of the area in contact. We tested our instrument by measuring the thermodynamic work of adhesion of a poly(dimethy siloxane) (PDMS) probe and slab, from which we obtained the surface energy of PDMS to be 21.5 mJ/m^2. The result is in close agreement with the literature value, and confirmed the validity of our construction.

COLL 211

Layer-by-layer assembled nucleic acid drug nanosponge for highly efficient drug delivery

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To achieve efficient drug delivery, a novel method for preparation of nucleic acid based carrier was developed. As carrier and drug, highly concentrated oligonucleotide (ODN) formed sponge-like nanostructure by enzymatic elongation without any crosslinker. The size of nanosponge dramatically decreased to favorable size for cellular uptake by a layer-by-layer assembly of

poly-L-lysine (PLL), DNA, and polyethyleninmine (PEI), without losing the amount of ODN. This LbL-coated nanosponge contained extremely high amount of ODN, $1X10^6$. In addition, LBL assembled nanosponge showed significant improvement of stability in *in vivo* environment and ability of endosomal escape.

COLL 212

Nanoindentation and nanoscratch profile influenced by the fabricated two–layer structure of silsesquioxanes and titanium tetrabutoxide

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Based on silsesquioxanes (SSO) derived from the hydrolytic condensation of (3-glacildoxypropyl)trimethoxysilane (GPMS), 20 wt-% tetraethoxysilane (TEOS) and titanium tetrabutoxide (TTB), two-layer SSO films were prepared for nanoindentation and nanoscratch tests. The tests were carried out to study the influence of different amounts of TTB in the two-layer hybrid films on hardness (H), elastic modulus (E) and scratch testing profiles. The H profiles of the modified films showed two kinds of H corresponding to the two–layer structure. In the scratch–testing profiles, all final–scan profiles did not absolutely coincide or overlap with the first–scan profiles. All scratch profiles revealed a fluctuanting characteristic and all scratch profiles can be divided into two regions in the horizontal displacement, because of the two-layer structure. The film containing an adequate amount of TTB (20 wt-%) was found to possess the largest H_1 (0.60 GPa) and E_1(9.23 GPa), as well as the best scratch resistance.

COLL 213

Preparation of core-shell typed TiO_2-polymer hybrid particles for electrophoretic display in non-aquous media

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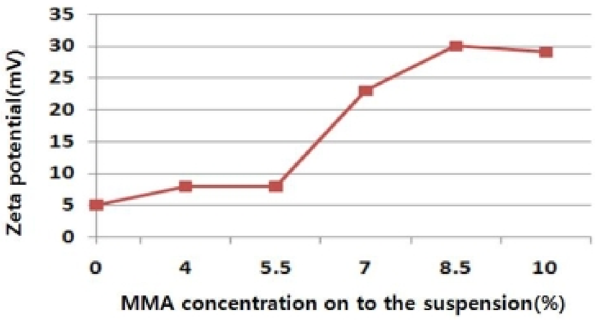
A new method of synthesizing the electrophoretic particles for a paper-like display is developed by dispersion polymerization in a non-aqueous media. The attempt to transfer the particle preparation from the convertional aqueous phase to non-aqueous phase provides the chance to fabricate a high mobility electronic ink without the electrophoretic particle milling process that is the energy consuming process. Nonionic surfactant was used as the steric stabilizer. The hybrid particles show high electrophoretic mobility values. Figure 1 show the suface stability transistion depending on the functionality of the hybrid particle surface.



COLL 214

Dielectric profiles of three polarized hybrids modified with tetraethoxysilicate

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Three hybrid materials (MST, VST and GST) based on (3-methacryloxypropyl)–silsesquioxane (MS), Vinyl–silsesquioxane (VS), (3-glycidoxypropyl)–silsesquioxane (GS) and modified with tetraethoxysilicate (TEOS) were prepared using hydrolytic condensation. The dielectric constant (ε_r) testing profiles of MST, VST and GST with 0, 5, 10, 15, 20 and 25 wt-% TEOS can be divided into three frequency ranges (0.10–21.54, 21.54–100.00 and 100.00–1000.00 KHz). MST has the lowestε_r because of the larger size of the methacryloxy groups, leading to the more homogeneous, porous and larger crosslinked network; GST has the highest ε_r because of the ring–opening of epoxy groups, leading to an incomplete crosslinked network and a greatly polarized structure. TEOS additions in the hybrids can decrease the ε_r but additional TEOS fractions can increase the ε_r . The hybrid containing 15 wt-% TEOS has the lowest ε_r due to an adequate amount of TEOS which produces an optimum porous structure and a denser crosslinked network.

COLL 215

Conformation of adsorbed citrate on gold nanoparticles: Intermolecular spacing and citrate bilayer

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The conformation of adsorbed citrate on gold nanoparticles (AuNPs) has been investigated. We employed attenuated total internal reflection-IR (ATR-IR) and x-ray photoelectron spectroscopy (XPS) to characterize coordination of the functional groups of the adsorbed citrates to the AuNP surface. Spectroscopy data indicates the central and one of the terminal carboxylate groups are associated with the surface binding, while the hydroxyl group is not involved in surface coordination. Also, the free carboxylate group exhibits *intraparticle-type* interactions with incoming metal ions. There is evidence of a second citrate layer interacting with the absorbed surface citrate through hydrogen bond formation between terminal free carboxylic acids, which form a citrate bilayer on the AuNP surface. The intermolecular spacing of the adsorbed citrate is estimated. We expect that more detailed characterization of the citrate adsorption on AuNPs will impact a broad area of AuNP-based studies including ligand exchange reactions, nanoparticle catalytic activity, and linker conjugation.

COLL 216

TPP-AuNPS in water: Stability and catalytic activity

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The effect of $NaBH_4$ and electrolyte concentration on the stability of TPP-AuNPs in water is presented. Electrons injected to this aqueous solution of AuNPs by $NaBH_4$ induce a red shift in the surface plasmon peak accompanied by a color change. However, aggregation of the NPs is not observed. A steady increase in the size of the AuNPs is observed, which is dependent on the amount of $NaBH_4$ added. XPS analysis shows that 53% of phosphorus is displaced from the AuNPs at the point where the red shift is at a maximum. Thereafter, a blue shift in the UV-Vis spectrum is observed. However, the original spectrum is not recovered. These TPP-AuNPs have been found to catalyze reduction of 4-nitrophenol by $NaBH_4$ as well as electron transfer reactions, for example, the reduction of hexacyanoferrate (III) by $NaBH_4$. These reactions show that these NPs can be used to remove pollutants from the environment.

COLL 217

Enhancing cell recognition by scrutinizing cell surfaces with a nanoparticle array

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We report a dual-ligand gold nanoparticle (DLGNP) array to discern the slight difference between cells that have different surface receptor profiles surrounding a common primary receptor. We synthesize DLGNP using folic acid as primary targeting ligand and the secondary ligand is made from a combinatorial array. Cell recognition is investigated in four cell lines with various expression levels of folate receptor (FR) and totally unknown receptor profile considering secondary receptors. Results display that cell binding and uptake of DLGNPs in different cells are quite different suggesting the different receptor profiles surrounding FRs. Furthermore, multivalent bindings of DLGNPs can differentiate cells with high and low expression of FRs and enhance the contrast between these cells in radiation-induced cell death measurements. These powerful enhancements of cell recognition and discrimination provide nanoparticles opportunities to treat patients at a personalized medicine level for drug delivery and radiation therapy with a much better safety profile.

COLL 218

Surface and gas phase chemistry of atomic layer deposition processes studied using tandem gas chromatography-mass spectrometry

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In order to improve existing atomic layer deposition (ALD) processes and develop new ones, it is desirable to understand the surface and gas-phase chemistry of the compounds used as precursors. In this work a novel approach is presented where that chemistry is characterized by using tandem gas chromatography-mass spectrometry (GC-MS). Less than a microliter of the metalorganic precursor is first placed in a glass vial capped with a septum and heated to the desired temperature in order to evaporate the precursor. Gas phase samples containing the reaction products are then extracted using a gas-tight syringe for GC-MS analysis. Samples from tetrakis-ethylmethylamido-titanium and tetrakis-dimethylamido-titanium, pure and in the presence of H_2O, revealed the formation of previously unreported tetramethylhydrazine and tetramethylmethanediamine, and reactions with pentakis-dimethylamido-tantalum yielded analogous results.

COLL 219

Improvement in the dispersion of silica nanoparticles

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The dispersion of 22 nm diameter silica particles in DMAC and in polyimide nanocomposites was studied by a combination of dynamic light scattering (DLS), transmission electron microscopy (TEM) and mechanical properties of the composite. Dispersion of the silica nanoparticles was aided by a thermally stable silane surface coating, which led to nanocomposites having well-dispersed particles and improved dimensional stability, as measured by the coefficient of thermal expansion (CTE). The surface modification to the particles was characterized by ESCA, elemental analysis, TGA and a colorimetric assay. The colorimetric assay for functional groups was found to be more sensitive than other analytical techniques. The synthetic route to the dye used in the colorimetric assay is discussed.

COLL 220

Synthesis and study of unsymmetrical phosphatidic acids designed to serve as 2D surfactants in Langmuir-Blodgett monolayers

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Line-active agents ("linactants") relieve surface tension and induce phase separation in chemically dissimilar mixed monolayer systems. This investigation explores the synthesis and study of a series of amphiphilic linactants having phosphatidic acid (PA) headgroups and semi-fluorinated and hydrocarbon tailgroups. We anticipate that Langmuir-Blodget monolayers composed of semi-fluorinated linactants will behave similarly to semi-fluorinated alkanethiols used in self assembled monolayers. These monolayers will be prepared from the targeted PAs, and their interfacial properties and phase behavior will be investigated by contact angle goniometry, atomic force microscopy (AFM), and Brewster angle microscopy (BAM). These linactants have been designed to offer control over the size of the phase-separated domains analogous to surfactants in corresponding three-dimensional systems. Keywords: Langmuir-Blodgett monolayers, Phase separation, Two-dimensional surfactant analog, Linactant

COLL 221

Preparation and characterization of SnO_2-coated metal nanoparticles embedded in tin oxide thin films

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Abstract: This presentation describes a sol-gel-based approach to the fabrication of tin oxide (SnO_2) semiconductor thin films in which metal nanoparticles are embedded. In this approach, gold nanoparticles with a mean size of ~15 nm were coated with a thin layer of SnO_2. The composite particles were ~50 nm in diameter with SnO_2 shells that were ~15-20 nm thick. These nanoparticles were doped homogeneously into a SnO_2 sol-gel precursor, and the mixture was deposited as a thin film using standard spin-coating methods. The SnO_2-coated nanoparticles and the SnO_2 films embedded with the nanoparticles were characterized by transmission and scanning electron microscopy (TEM and SEM) and X-ray diffraction (XRD). The optical properties of the nanoparticles and the composite films were evaluated by UV-vis spectroscopy. Importantly, the surface plasmon resonance arising from the gold-nanoparticle-doped SnO_2 films was clearly detectable, exhibiting a red shift when compared to unmodified gold nanoparticles.

COLL 222

Role of salt in the spontaneous assembly of charged gold nanoparticles in ethanol

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This research investigates the role of salt in the spontaneous assembly of charged gold nanoparticles in ethanol , and tries to clear up a misunderstanding on ethanol effect in this process. In lots of literature, ethanol was considered as a main factor to make charged gold nanoparticles aggregated. However, after an elaborate exploration of the assembly by UV-Vis, TEM, and DLS, we found that it is the residual salt, instead of ethanol itself, which induces the linear aggregation of the gold nanoparticles in ethanol due to the decrease of electrostatic repulsion force interparticles. Further, we found that the chainlike aggregates triggered by salt could dissociate by diluting salt concentration or evaporating the ethanol in it. We expect this work can cast some light on the mechanism of spontaneous assembly of nanoparticles in ethanol.

COLL 223

Behaviors of cyano-stilbene derivatives at the air-water interface

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π-conjugated organic molecules opens up new possibilities such as nanoscale biological and optoelectronic devices and can be controlled optoelectrical properties easily because of the concentration-fluorescence quenching phenomenon that occurs when fluorescent organic materials aggregate. Trans-stilbene derivatives are one example of fluorescent organic molecules and are appeared that 'unit aggregate' and the extended array in films, the nearest neighbors show an edge-to-face arrangement. Fluorescent probe molecules, (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4-butoxyphenyl)acrylonitrile) (DBDCS) and (2Z,2'Z)-2,2'-(1,4-phenylene)bis(3-(4'-(2,5,8,11,14,17,20,23,26,29,32,35,38,41,44,47,50-heptadecaoxadopentacontan-52-yloxy)biphenyl-4-yl)acrylonitrile) (17EO-CNBPST), at the air-water interface and Langmuir-Blodgett film have been investigated by $\mathbf{\Pi}-A$ isotherm, AFM, STM, and X-ray reflectivity. If material expose to UV and visible light, cis/trans isomerization of cyano-stilbene can be occur in solution. As a result of this, $\mathbf{\Pi}-A$ isotherms of different shape are observed in different light conditions (light off, UV 254nm, and daylight). From fabricated monolayer films, nano-sheet structure due to the arranged aggregation was shown by AFM.

COLL 224

Separation of pharmaceuticals by selective surface adsorption

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Mobile condensed matter (MCM) are a known[i] class of sol-gel materials prepared by mixing a solution of silica and a surfactant together and polymerizing the silica in a sol-gel process, where silica polymerizes around the surfactant micelles and afterwards undergoes a hardening process known as gelation. MCM-41 possesses hexagonally packed arrays of channels with very high surface area and narrow pore size distribution compared with amorphous silica, whereas MCM-48 are cubic packed arrays with a 3-D array of pores, where the silica/surfactant ratio determines the symmetry of the pores. MCM sol-gel materials can be functionalized[ii] by synthesizing the silica with an organic side chain, in order to achieve specific chemical interaction in the pores. Herein we report the synthesis of a nonafluorohexyl functionalized porous sol-gel material, which exhibits selective adsorption of molecules with close chemical structure and properties. Complimentary Isothermal titration calorimetric (ITC) and Quartz crystal microbalance measured the adsorption isotherms of the organic

molecules to our functionalized silica material. Binding constants for the different molecules were obtained indirectly from our adsorption curves, and demonstrated their selectivity towards the porous material. Future prospects for these functionalized silica materials is to incorporate them in a separation step between the active pharmaceutical ingredient (API) and impurities in a continuous manufacturing process of the desired drug compound. [i] J. S. Beck, et al. Journal of the American Chemical Society, 114 (1992) 10834 [ii] M.H. Lim et al. Journal of the American Chemical Society, 119 (1997) 4090

COLL 225

Remotely on-off switchable on-demand drug release

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Nanoparticle based delivery is of particular interest for potential controlled-release, drug vehicles. Here we prepared ~100 nm diameter hollow nanocapsules containing intentionally trapped magnetic nanoparticles and defined anticancer drugs such as camptothecin and doxorubicin to allow a controlled on-off switchable release of the drug cargo via remote RF field. The mechanisms involved in the observed switchable drug release were investigated. Remotely applied magnetic field induces the associated drug molecules to be released from the nanosphere on-demand. The rate of diffusional drug release is controllable by the degree and duration of magnetic field as well as the chemistry and structure of the capsule materials involved. This smart drug delivery system is compact as all the components can be self-contained in 80~150 nm capsules. *In vitro* results indicate that these nanocapsules are effective in reducing tumor cell growth.

COLL 226

Roughness influenced deposition of latex colloids at mineral surfaces: An analog study

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As an analog to rough mineral surfaces with halfpores in the submicron size, the deposition behavior of latex colloids on a well-defined, structured silicon wafer

surface was investigated. The topography consists of a regular pit pattern (pit diameter=400 nm, pit spacing=400 nm, pit depth=100 nm). The influence of particle diameter variation (from the range of 0.3-2 µm) on retention of monodisperse as well as poly-disperse suspensions, as a function of flow velocity over a wide range was studied. Despite electrostatically unfavorable conditions, at all flow velocities, a significant retention of colloids was observed at the rough vs. smooth (Rq~18 nm vs. 1.6 nm) substratum. The effect of surface roughness was found to be more significant for smaller colloids (0.3 and 0.43 µm). From smooth to rough surfaces, the deposition rate of 0.3 and 0.43 µm colloids increased by a factor of approx. 2.7 compared to a factor of 1.2 or 1.8 for 1 and 2 µm colloids, respectively. For a substrate herein, with constant surface topography, the ratio between substrate roughness and radius of colloid, Rq/r_c, determined the deposition efficiency. As Rq/r_c increased, particle-substrate interaction energy decreased. Larger colloids (1 and 2 µm) beyond a critical velocity (7×10^{-5} and 3×10^{-6} m/s) (when drag force exceeds adhesion force), tend to detach from the surface irrespective of the impact of roughness. For polydisperse solutions, an increase in the polydispersity and flow velocity resulted in the decrement of colloid deposition efficiency due to the enhanced double layer repulsions.

COLL 227

Microwave-assisted modification of montmorillonite by novel gemini surfactants

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COLL 228

Investigation of adsorption of gelatin on the surface of polyurethane elastomers by a viscometric method

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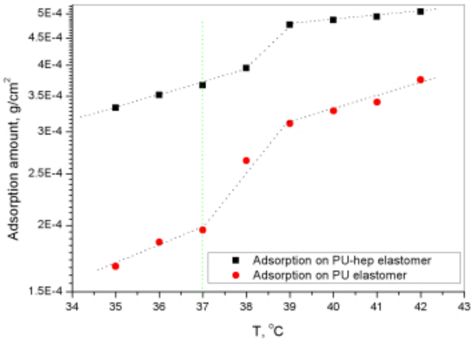
A special IPDI type polyurethane (PU) elastomer and heparin grafted PU elastomer (PU-hep) were prepared.The adsorption of gelatin on the surface of PU and PU-hep elastomers was investigated from experimental relative viscosity data using a viscosity equation with interfacial effect correction. The result showed that in the range of 35□~42□, gelatin macromolecules were easy to be adsorbed on the surface of the PU elastomer, and the PU-hep elasomer showed larger adsorption capacity.



COLL 229

Synthesis and characterization of large silica-coated gold nanoshells

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This report describes the structural and optical properties of multilayer nanoshells having a silica core (~850 nm diameter) coated with a gold shell (~50 nm thickness), which is further coated with a silica shell (~100 nm thickness). These nanoparticles are being developed for use as near IR responsive materials that are both chemically inert and thermally stable. The size and morphology of the composite nanoparticles were examined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The composition of the particles was evaluated by Fourier-transform infrared (FT-IR) spectroscopy and powder X-ray diffraction (XRD), while the optical properties were characterized by UV-Vis-NIR spectroscopy. These characterization tools collectively show that large multilayer nanoshells can be reproducibly prepared in monodisperse form; moreover, these robust composite nanoparticles exhibit strong absorptions in the near IR.

COLL 230

Properties of cationic birchwood xylan layers adsorbed on cellulose model films studied by QCM-D

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The adsorption of cationic modified birchwood xylan (CX) with different degree of substitution on cellulose model surfaces was examined using quartz crystal microbalance with dissipation (QCM-D). Hydrophobised cellulose (trimethylsilyl cellulose, TMSC) was coated by spin coater on the hydrophobic, polystyrene-coated QCM-D crystal, after which the TMSC was regenerated back to cellulose by vapour phase acid hydrolysis (10%). Ultra thin cellulose films were characterized using atomic force microscopy (AFM) and electron spectroscopy for chemical analysis (ESCA) to determine the thickness and chemical structure of the layers. The amount of CX adsorbed layers can be calculated using the Sauerbrey equation. However, when thick and soft layers in liquids were formed between cellulose films and CX, the conformation and viscoelastic properties of the layers were interpreted by modelling the data assuming that the layers can be explained as a Voigt model. The adsorption of the CX with low charge density to the cellulose surface was relatively weak and CX formed a thick and soft layers with higher elasticity and thickness than the layers formed by high charged CX, which means that more roof-tail conformation was formed.

COLL 231

Pseudo-polyelectrolyte, poly(4-vinylphenol), as an antimicrobial multilayered surface coating

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Weak polyelectrolytes in multilayer polymer systems provides a means of altering the physico-chemical properties of these thin films. We examined the limits of the polyanions by incorporating the pseudo-polyelectrolytes (pPE), poly(4-vinylphenol) (PVPh), into multilayer systems with either the weak polyelectrolyte (WPE), poly(allylamine hydrochloride) (PAH) and the strong polyelectrolyte (SPE), poly(diallyldimethylammonium chloride) (PDADMAC) from dilute aqueous media. Since PVPh exhibits moderate antimicrobial ability, we tested these multilayered systems to determine their ability to act as antimicrobial surface coatings. The PAH/PVPh system showed approximately 60% inhibition of growth under nutrient rich environment for *Staphylococcus epidermidis* when assembled at pH's 10.5 and 12.5. At assembly pH's between this range there was a decrease in efficacy. For the PDADMAC/PVPh multilayered coatings, >70% inhibition of growth of *S. epidermidis* was observed at an assembly pH of 10.5

and 11.0. This represents the first example of multilayered PVPh being used as an antimicrobial surface coating.

COLL 232

Fabrication of nanostructured inorganic materials by self-assemblies of diblock copolymers

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Diblock copolymers composed of two different polymers can be coated onto substrates by spin-coating to obtain self-assembled periodic nanostructures via thermal annealing and solvent vapor treatment. The size and morphology of diblock copolymers can be easily controlled by the molecular weight and composition of copolymers. Due to facile creation of nanopatterns over large area with low cost, there has been numerous researches conducted on self-assembled thin films of diblock copolymers which can serve as nanoscale lithographic masks for etching processes and nanotemplates to generate nanomaterials such as nanoscale cylinder/lamella arrays and nanoporous films. In this presentation, we will demonstrate various morphologies in diblock copolymer films produced by thermal and solvent annealing to create diverse nanostructured metals and metal oxides, which are potentially useful for optoelectronic applications such as ordered nanoelectrodes for hybrid photovoltaic devices.

COLL 233

Preparation of colloidal silsesquioxane particles from bridged monomer under acidic conditions

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Hybrid organic-inorganic particles with precise controlled size and size distribution have attracted considerable interest due to their various applications in chromatography, coatings, catalysts, and optics. Traditional “Stöber” method is an excellent procedure to synthesize monodispersed spherical particles from tetrafunctional silane monomer under basic conditions. However, we tried to prepare colloidal hybrid particles from the bridged silsesquioxane monomer using the same “Stöber” conditions and results showed no particles were generated. In this paper, spherical colloidal particles can be instead produced from the same silsesquioxane monomer under acidic conditions. We investigate the particle

growth following the time and results showed particle size and growth rate were dependent on the monomer concentration. Dynamic light scattering, scanning electron microscopy and other techniques will be employed to characterize the synthesized hybrid colloidal particles in this work.

COLL 234

Effect of polymer adsorption kinetics and ionic strength on poly-dispersed colloidal flocculation dynamics

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This study reports new findings on how the cationic polyacryamide (CPAM) adsorption kinetics and the ionic strength affect the flocculation kinetics of a poly-dispersed calcium carbonate (CC) suspension. The full CC flocculation kinetics were measured by combining the Photometric Dispersion Analyser and the Focused Beam Reflectance Measurement. The polymer adsorption kinetics were quantified by subtracting the CPAM concentration in the supernatant after adsorption from the initial concentration. The time scale of polymer adsorption and colloidal flocculation equilibrium for this system was comparable. We observed disobedience of the surface coverage theory for flocculation rate based on the monolayer adsorption model. All early flocculation happened under non-equilibrium polymer adsorption regimes. Polymer adsorption kinetics and the transient polymer conformation overrode its adsorbed amount in controlling colloidal flocculation. Unexpected synergistic effect of salt and polymer on flocculation was recorded; this new finding promises potential to optimize flocculation conditions by only manipulating the engineering process.

COLL 235

Directed ceramic condensation via Silicatein α inspired block copolymer

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A bio-mimetic polymer, poly(hydroxylated butadiene-*b*-2-vinylpyridine), was used as a template for the condensation of titania using titanium(IV)i-propoxide as the precursor. The structure of our polymer is based on two amino acid residues shown to be key for hydrolysis of tetraethoxysilane (TEOS) under ambient temperature and near-neutral pH by Silicatein α. Our work has resulted in the growth of titatnia on a mimic copolymer spin coated slide by dipping the slide in

the titania precursor. Previously, this mimic copolymer was demonstrated to have the ability to condense silica using TEOS as a precursor. We have used TGA, FESEM, and AFM to characterize these films. Applications of this work include the construction of a more efficient dye-sensitized solar cell and will also include functionalized graphene sheets (FGS) incorporated in the titania layer.

COLL 236

Preparation of various gold and silver nanoparticles by fluorescent light irradiation

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The preparation of various sizes of gold and silver nanoparticles was accomplished using trisodium citrate as a reducing agent at room temperature under fluorescent light irradiation. The resulting nanoparticles were thoroughly characterized by UV-visible spectroscopy, scanning and transmission electron microscopy, and dynamic light scattering. While the size of silver nanoparticles was remained constant, the diameter of gold nanoparticles (from ~20 nm to ~200nm) was systematically controlled by the concentrations of the reducing agent. This photochemical reduction is the first time to demonstrate that the reliable preparation of gold and silver nanoparticles at room temperature upon irradiation of fluorescent light.

COLL 237

Sum frequency vibrational spectroscopy study of the interaction of Hofmeister ions with hydrophilic surfaces

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Surface sensitive vibrational sum frequency spectroscopy has been used in our laboratory to investigate the effect of Hofmeister ions on model hydrophilic surfaces such as quartz and titanium oxide. This was done in order to understand the interaction of both anions and cations with interfaces where the surface charge state is one of the main variables dominating the interaction. Solutions from various sodium and chloride salts were introduced into a flow cell to make contact with a particular solid substrate. Generally the effect of anions was more pronounced than that of the cations in biologically relevant systems.

However, from the results of our experiments with hydrophilic inorganic surfaces, the effects of the cations are as prominent as the effects of the anions.

COLL 238

Diffusion dynamics of combination of drugs in hydrogels

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Hydrogels are smart drug delivery system that can respond to a variety of physical, chemical and biological stimuli. However, the potential of hydrogels as a novel drug delivery system of combination of therapeutics has not been explored in detail. The main objective of our research project is to understand transport and diffusion kinetics of different combination of drugs in hydrogels. We have synthesized and characterized copolymer hydrogels using N-isopropyl acrylamide and acrylic acid. We were able to relate the low critical solution temperature, microstructure and the swelling properties of the different chemical composition of hydrogels. The microstructure, studied scanning electron microscopy, was also examined to understand the diffusion kinetics of different drug candidates that were chosen for this study (aspirin, warfarin, acetaminophen).

COLL 239

Chemical liquid deposition of π-conjugated polymer films based on Schiff base couplings

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Materials for organic electronics, especially π-conjugated polymer films, have been extensively researched from both fundamental and industrial perspectives because of their unique electronic and optical properties. Herein, a novel chemical liquid deposition strategy for the preparation of π-conjugated aromatic polymer films is proposed. The films are produced through a soft solution process based on an adsorption-induced equilibrium for polycondensation at the solid-liquid interface created by deliberately suppressing the polycondensation

reaction in solution. This “on-site” synthetic methodology allows the formation of ultrathin polymer films consisting of extended linear π-conjugated aromatic polymers from aqueous solution under ambient conditions. Additionally, this soft solution methodology eliminates the necessity for harsh preparation conditions, such as high temperature or low pressure, common to most current fabrication techniques.

COLL 240

Role of surface charge in specific cation effects

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Interactions of cations with a charged peptide and its impact on interfacial water structure were investigated using vibrational sum frequency spectroscopy (VSFS). An elastin-like polypeptide was adsorbed at air-water interface. The presence of multiple titratable aspartic acid residues imparted a very dramatic change in interfacial water structuring upon change in pH. The effects of the presence of a series of chloride salts on this water ordering were recorded and the resulting trends were explained in terms of a cation's relative affinity for polar/hydrophobic moieties on the polypeptide. This study gives molecular level details of how cations interact with charged biomacromolecules and the reported findings will help to better understand phenomena like Hofmeister effects, ion channel chemistry and biofouling processes.

COLL 241

Co-adsorption of alcohol and water on SiO-$_2$ in ambient conditions: Sum-frequency-generation (SFG) vibration spectroscopy and attenuated internal reflection (ATR) infrared spectroscopy studies

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This study elucidates the structure of the co-adsorbed layer of water and alcohol on silicon oxide surface in ambient conditions. The competitive adsorption of water and alcohol molecules is an important factor affecting the vapor phase lubrication of oxide surfaces with alcohol molecules in humid air. Here, the structure, orientation, and adsorption isotherm of co-adsorbed n-alcohol and water molecules on silicon oxide were studied using sum frequency generation vibration spectroscopy (SFG) and attenuated total reflectance infrared

spectroscopy (ATR-IR). It was found that the composition of the adsorbed alcohol on silicon oxide surfaces is significantly difference from that of the liquid/air interface. It also varies depending on the water-alcohol miscibility. Also, the co-adsorbed n-alcohol molecules influence the structure of the adsorbed water layers.

COLL 242

One-step production of superhydrophobic coatings on flat substrates via atmospheric rf plasma process using non-fluorinated hydrocarbons

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This paper describes the direct deposition of hydrocarbon coatings with a static water contact angle higher than 150° using simple C6 hydrocarbons as a reactive gas in helium plasma generated in ambient air without any pre-roughening of the silicon(100) substrate. The film morphology and hydrophobicity are found to strongly depend on the structure of the reagent hydrocarbon. The films deposited with n-hexane and cyclohexane exhibited relatively smooth morphology and the water contact angle was only ~95°, similar to polypropylene. When benzene was used as a main reactive gas, the deposited film surface showed nano-scale textured morphology and superhydrophobicity with a water contact angle as high as 167°. Since the plasma is generated in air, all films show some degree of oxygen incorporation. These results imply that the incorporation of a small amount oxygenated species in hydrocarbon films due to excitation of ambient air is not detrimental for superhydrophobicity, which allows the atmospheric rf plasma with the benzene precursor to produce rough surface topography needed for superhydrophobicity.

COLL 243

NMR investigation of phospholipid/PEG-ceramide-liposomes

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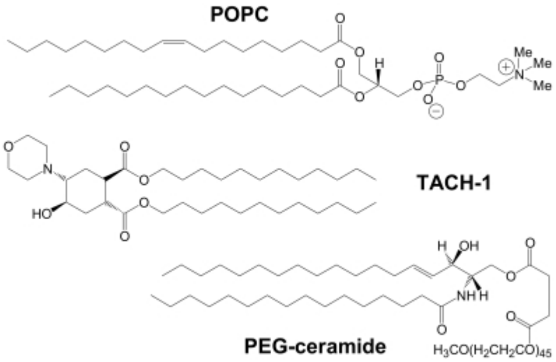
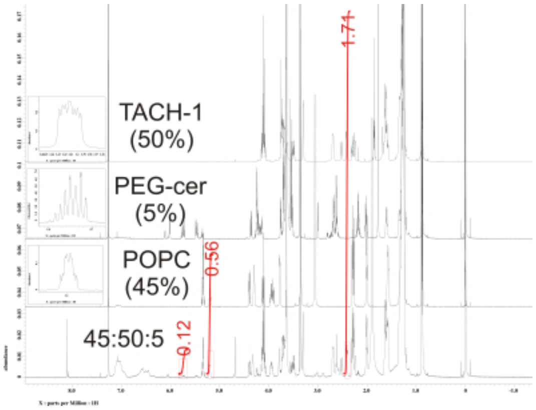
Liposomes are macromolecular structures in which an aqueous core is surrounded by a double-layered lipid membrane. Surface modifications in

liposomes serve the purpose of enhanced water-solubility, immuno-compatibility, and targeted delivery of liposome “cargo”, e.g. drugs or DNA/RNA. Liposomal drug delivery systems are frequently composed of phospho-lipids and ceramides amongst others.



We investigated pH-sensitive liposomes. Complete NMR structure assignment and quantification of all components provided quality control. During liposome extrusion/preparation/loading and cleanup, little to no variation in composition was observed.



COLL 244

Nanomaterial base diagonosis and nanotherapy of lever cancer cells

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Lever cancer is the leading cause of cancer-related death among the American population and the cost of treating prostate cancer patients is about $12 billion/year in the US. Current treatments are mostly ineffective against advanced stage prostate cancer disease and are often associated with severe side effects.

Here we will discuss, our recent report on multifunctional nanotechnology-driven approach for targeted sensing and nanotherapy treatment of lever cancer cells.

COLL 245

pH-Sensitive liposomes with new *trans*-2-aminocyclohexanol-based amphiphiles as conformational switches for the liposome membrane

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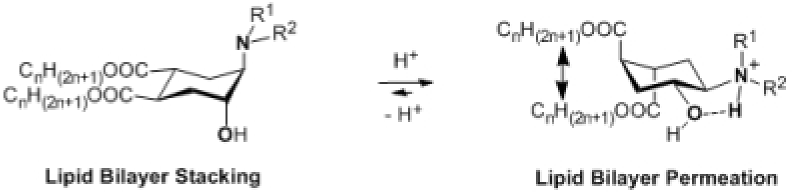
We suggested recently a novel approach to making lipid amphiphiles and their colloids pH-sensitive: a protonation-induced conformational switch of the built-in *trans*-2-aminocyclohexanol moiety. In liposomes, this ring flip loosens packing of the attached lipid tails, leading to contents leakage. Here we report our latest studies on the pH-sensitivity of PEG-grafted liposomes containing various *trans*-2-aminocyclohexanol-based lipids in their membranes. These liposomes are stable at pH 7.4 and yet release their content in a few seconds in a slightly acidic medium. The triggering pH value depends on the structure of amino-group.



COLL 246

Pentacene thin films on vicinal Ag(111) surfaces

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Here we present our theoretical and experimental studies regarding pentacene thin film formation on vicinal Ag(111) surfaces. Helium difrraction results indicate a step flow film growth mechanism: The length (slope) of the initial slow decay region in specular reflection intensity vs. deposition time curves decreases (increases) as the surface step density decreases. This is in agreement with our DFT calculations, where pentacene is found to adsorb strongest parallel to the sted edge in a tilted fashion.

COLL 247

PEG-based liposome stabilization using DNA-lipid conjugates

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Liposomes—artificial phospholipid bilayers—are widely used as model systems for biological membranes. For example, this lipid-based model system can be used for screening molecules that interact with G protein-coupled receptors (GPCRs). Since fragility and short life time limit the applicability of liposomes, we have developed a novel platform based on hydrogel-containing nanoscale liposomes assemble by DNA hybridization with enhanced stability and longevity. We constructed stable liposomes by encapsulating a UV-initiated poly(ethylene glycol) (PEG) hydrogel in liposome which is bound to the lipid bilayer through DNA hybridization. We developed two approaches for making DNA-containing liposomes. In one approach, we synthesized a DNA-modified lipid that can hybridize with its vinyl-modified complementary sequence, which is incorporated in the hydrogel during polymerization. In another approach, we incorporated double-stranded DNA-modified cholesterol in the bilayer; the complement of the cholesterol-conjugated strand contained a vinyl group that was incorporated in the hydrogel. To confirm hybridization of DNA in liposomes, we used a fluorophore sensitive to double-stranded DNA. Fluorescence was enhanced noticeably upon binding to hybridized DNA, while no fluorescence was measured in liposomes with only single-stranded DNA. Using dynamic light scattering and electron microscopy, we confirmed the stabilization of DNA-anchored liposomes.

COLL 248

Universal photografting method of nanoparticle-films on hard and soft substrates

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The ability to control surface properties is important to a wide range of applications from increasing throughput signals on biodiagnostic devices to improving the wear resistance of superhydrophobic coatings on aircraft vehicles. Many efforts have focused on modifying surfaces with nanoparticles (NP) because of their distinctive advantage in large surface area to volume ratio. However, current NP-film preparation methods are not well-developed. Our research corroborates a two-fold photochemical method that is universal and has high spatial selectivity in grafting - (1) a "grafting-to" approach where the photoactive linkers are functionalized on the NP (e.g. Silica) and (2) a "grafting-

from" approach where the photoactive linkers are self-assembled as a monolayer onto the substrate (e.g. glass). With surface techniques, such as Confocal Fluorescence Microscopy, X-ray Photoelectron Spectroscopy, and Scanning Electron Microscopy, we are able to measure the spatial selectivity (NP-photopatterned), atomic composition, density, and wear resistance of these NP-functionalized surfaces.

COLL 249

Correlation of interfacial molecular structure and dynamic properties of PDMS fluids on Ag and SiO_2

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Exploration of the molecular structure-function relationships that influence the fluid dynamic properties within interfaces are necessary for many modern applications in devices and coatings. Forced dewetting with post-spectral probing is a strategy that allows physical isolation and examination of solid-fluid interfaces without spectral interference from the bulk fluid. In this work, SiO_2 and Ag substrates were forcibly dewet from polydimethylsiloxane (PDMS) oligomers of varying length and viscosity under N_2 or PDMS-saturated conditions. Residual PDMS films created by this process were investigated using ellipsometry, polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS), transmission infrared spectroscopy, and contact angle measurements to determine how molecular interfacial structure and PDMS orientation affect the static and dynamic properties of the interfacial polymer. Results are compared to film thicknesses predicted by both a purely long range force Lifshitz model and a purely hydrodynamic force model (Landua-Levich-Dejaguin). Across a series of PDMS oligomers ranging from MW of 162 to 950, control of residual layer thickness changes from long range forces for the lower MW PDMS species to hydrodynamic forces for the higher MW species despite the relatively small change in viscosity across this PDMS fluid series. These studies suggest that hydrodynamic control of film formation may be reinforced by molecular entanglement of the longer PDMS oligomers.

COLL 250

Reactions of low work function metals with ordered carbon forms using surface Raman spectroscopy

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It has previously been shown from this laboratory that the formation of small amounts of graphitic-like carbon occurs as a common endpoint in reaction chemistry that occurs during the vapor deposition of low work function (Φ) metal contacts (e.g. Ag, Ca, Al and Mg) on solid-state organic thin films. The presence of even small amounts of such graphitic-like carbon has significant implications for interfacial electronic structure and device performance in organic light emitting diodes, organic photovoltaics, and organic transistors. Therefore, it is imperative to further understand the reaction pathways that produce these graphitic-like carbon forms during the formation of ohmic contacts from such metals. Toward this end, ultrahigh vacuum (UHV) surface Raman spectroscopy has been used to define the evolution of interfacial chemistry upon vapor deposition of low Φ metal contacts on ordered carbon forms such as graphene and C_{60}. Reactions initiated by metal-to-organic electron transfer are proposed which lead to further degradation and polymerization of these carbon forms. These results will be discussed and the relevant device implications considered.

COLL 251

Tunable thin film water structure via changing terminal SAM functionality

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Solvent molecules at interfaces often display distinct structure and bonding interactions when compared to the surrounding bulk phases. Understanding the implications of this behavior on broader chemical systems is becoming an area of great importance across many disciplines. In this study, we present the interfacial structure of thin films of water (D_2O) on well defined alkanethiol SAM-modified Ag substrates with surface chemistries systematically varying from hydrophobic (alkanethiols with $-CH_3$ terminal groups) to hydrophilic (alkanethiols with -OH terminal groups). Varying degrees of hydrogen bonding are achieved through use of mixed monolayers of these differently-terminated alkanethiols to create surfaces with contact angles from ranging from $\sim 110° > \theta > 30°$. Thin fluid films are created either by surface condensation or by highly-controlled dynamic dewetting of the surface from a liquid droplet. The resulting films are probed by ellipsometry and PM-IRRAS. Results for layer thicknesses and the vibrational structure of the films are compared with quantitative simulation as a function of SAM surface composition/hydrophobicity. Several unique interfacial water environments are identified in the spectral results, and evidence for condensation by microfluid-droplet formation as a precursor to contiguous films is presented.

COLL 252

Geometric effect in the micellization of aqueous solutions of rhamnolipid biosurfactant mixed with Tween-20

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The synergetic behavior of mixed surfactant systems has been widely utilized in industrial and technological applications for enhanced performance and low production cost. In this work, the solution behavior of monorhamnolipid, a biosurfactant produced by *Pseudomonas aeruginosa*, was investigated in mixtures with the nonionic surfactant Tween-20. The critical micelle concentrations (CMC) of monorhamnolipid, Tween-20 and their mixtures have been measured using surface tension measurements at pH 8. These measurements show that the addition of Tween-20 to monorhamnolipid solutions shows non-ideal mixture behavior, with the CMC reaching an unexpected minimum at a Tween-20 mole fraction in the vicinity of 0.2. However the CMC shifts to larger values as the mole ratio of Tween-20 increases. This micellization behavior can not be explained by a simple model based on the reduction of electrostatic repulsion, but is well explained as a geometric effect of surfactant packing. Geometric control of micelle structure is further confirmed by the results of dynamic light scattering, which shows a transition from rod-shaped micelles for pure monorhamnolipid to increasingly spherical micelles as the mole fraction of Tween-20 increases.

COLL 253

Effects of polymeric additives on the transfomation of calcuim phosphate crystals

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Interactions of fluoride ions with calcium phosphate crystals have attracted many attentions mainly because of their biomedical implications. Calcium phosphates in contact with fluoride ions usually transform into fluorapatite in aqueous environments. In the present work, pure hydroxyapatite (HA), octacalcium phosphate (OCP), and dicalcium phosphate dihydrate (DCPD or brushite) were prepared, and the synthesized crystal phases have been confirmed by scanning electron microscopy (SEM) and wide angle X-ray diffraction (WAXD). The obtained calcium phosphate crystals have been exposed to sodium fluoride

aqueous solutions to study kinetics of the phase transformations. In addition, the effects of polymeric additives on the transformation kinetics was examined to enable biomimetic regulation of crystallization.

COLL 254

Simultaneous control of molecular weight and tacticity of thermoresponsive polymer brushes by surface-initiated living radical polymerization

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In this study, thermoresponsive poly(N-isopropylacrylamide) (PNIPAAm) brushes were grafted from surfaces by living radical polymerization to simultaneously control their molecular weight and tacticity. PNIPAAm brush surface was prepared by surface-initiated ATRP in the presence of $Y(TOf)_3$, and the optimized conditions for controlling tacticity and molecular weight were found. Addition of $Y(OTf)_3$ in the surface-initiated ATRP of PNIPAAm increased the meso dyad content of polymer brushes, and tacticity was controlled by varying $Y(OTf)_3$ concentrations. The polymerization temperature and monomer concentration in ATRP in the presence of $Y(OTf)_3$ were available factors for controlling the molecular weight of PNIPAAm brush with a high isotacticity. The effect of PNIPAAm brush tacticity on the thermoresponsive wettabiliy was investigated by contact angle measurement. The wettability of isotactic PNIPAAm brush surfaces decreased slightly below 10 °C, and this temperature response is different from not only the atactic polymer brush surfaces, but also for isotactic bulk polymers.

COLL 255

Effects of surface chemistry on ionic liquid droplet formation in a microfluidic device for reaction synthesis

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A passive method for creating monodisperse ionic liquid droplets in a microfluidic device is presented. This PDMS device utilizes channel geometry along with surface chemistry modifications to facilitate the difficult breakup of the highly viscous ionic liquid. Prefabricated microchannels were modified using initiated chemical vapor deposition (iCVD) of poly(1H,1H,2H,2H-perfluorodecyl acrylate) (PPFDA). This is the first reported application of iCVD on a completed microchannel. The fluorinated channel promotes wetting by a continuous fluorous phase. This carrier fluid encapsulates micron sized droplets of the dispersed phase, ionic liquid solutions. Well controlled droplet formation is critical for its use in forming reaction vessels for metal nanoparticle synthesis.

COLL 256

Interaction of lipidic wrapped carbon nanotube with lipid monolayer at air-water interface

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In the applications CNT in biological applications, understanding of interactions between CNT with cell surface is crucial for the design of bio-functionalized CNT's in an efficient way. In this study, we prepared single-walled carbon nanotube (SWNT) wrapped with 1-stearoyl-2-hydroxy-sn-glycero-3-phospho-(1'-rac-glycerol)(LPG) under the ultrasonic irradiation, leading to a composite system of SWNT/LPG. In order to investigate the interaction of SWNT/LPG with cell surface, monolayer of dipalmitoylphosphatidylcholine (DPPC) was adopted as a model system. Aliquots of SWNT/LPG were injected into the aqueous subphase to induce the insertion of SWNT/LPG into the lipid monolayer. Changes in the interaction between the functionalized CNT and DPPC monolayer were monitored by area change for a specified surface pressure. Variations of surface potential were also measured to more clearly trace the various modes of interactions between subphase and monolayer.

COLL 257

Pickering emulsion polymerization process as a convenient synthesis route in the fabrication of armored polymer latexes

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The fabrication of polymer dispersions using a waterborne process is of great industrial relevance with applications in coatings, adhesives, printing inks, asphalt, etc. Materials properties and performance can be enhanced

incorporating fillers into these polymer latex dispersions. We recently demonstrated that using “soft” latex particles armored with a layer of inorganic particles as additive in waterborne pressure sensitive adhesives led to a marked increase in the tack adhesion energy. However the fabrication of these polymer nanocomposites is not clear. For example, a blend of a “soft” polymer latex and a nanosized clay sol did not lead to an improved waterborne pressure sensitive adhesive. Therefore, there is a clear need to design more complex polymer particles. Herein, we have developed a Pickering emulsion polymerization process as a convenient synthesis route in the fabrication of armored polymer latexes. Additionally polymerization kinetics and mechanism formation of armored polymer latex particles are investigated.

COLL 258

Fabrication and characterization of phosphonic acid monolayers for use in biosensing

Kristi L Liddell(1)*, klb456@psu.edu, 104 Chemistry Building, University Park PA 16802, United States ; Christine D Keating*(1)*; Xiahua Zhong*(2)*; Theresa S Mayer*(2)*; Stacey L Dean*(1)*; Kaige Sun*(2)*. (1) Department of Chemistry, Pennsylvania State University, University Park PA 16802, United States (2) Department of Electrical Engineering, Pennsylvania State University, University Park PA 16802, United States*

@font-face { font-family: "Cambria"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 0.0001pt; font-size: 12pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } Silicon nanowire field-effect transistors (FETs) have the potential to combine powerful microchip computing with biological samples to produce a highly sensitive and multiplexed sensing device. Despite the convenient fabrication of silica for the gate dielectric, significant problems for chemical detection in solution still remain. Understanding DNA hybridization on alumina or other metal oxides is of interest as this has been extensively studied on silica but is less understood with other materials. Organosilanes are the most common route to chemically modify metal oxide surfaces for coupling bioactive molecules such as biotin, DNA, or PNA. Alkyl phosphonic acids can form self-assembled monolayers (SAMs) on a variety of non-silica metal oxides and demonstrate increased stability at physiological conditions, compared to traditional silanes. This poster will describe fabrication and characterization of phosphonic acid monolayers on metal oxide surfaces for biomolecule coupling on FETs.

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Reactions between “unreactive” silicones and metal oxide surfaces

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Reactions of silicones with metal oxide surfaces were studied and surface-initiated siloxane bond hydrolysis was observed to be general among various metal oxides. Stable hydrophobic surfaces with reproducible surface properties were prepared on a range of solid substrates. In particular, trimethylsilyl-terminated poly(dimethylsiloxane)s, which do not have an obvious reactive site, show good reactivity with a wide range of metal oxides. Linear and cyclic silicones, with and without functional groups, are shown to create surfaces with defined properties on titania, silica, alumina, and nickel oxide surfaces (with various topographies and topologies). A surprisingly simple and reproducible technique for preparing hydrophobic surfaces displaying low contact angle is described.

COLL 262

Insights into the effect of unsaturations in the surface structure of fatty acids monolayers and its interfacial aqueous subphase: A vibrational sum frequency spectroscopy study

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Vibrational Sum Frequency Spectroscopy (VSFS) has been used to study changes in the conformational order of fatty acid (Arachidic Acid – AA and Eicosenoic Acid – EA) films spread on a Langmuir trough. The presence of fatty acid-rich domains floating in equilibrium with pure water patches were observed for both films at areas per molecule larger that the lift-off surface pressure. Moreover, it was determined that the domains were of crystalline nature for AA, while they were isotropic and less ordered for EA. This conformational disorder initially found on the domains of EA was seen to continuously decrease upon monolayer compression. At pH~6 it was determined that the fatty acid head group for either monolayer is essentially uncharged in pure water, as well as in the presence of NaCl in the subphase. A dramatic increase was however observed in the signal of the water hydrating the headgroups indicating a

preferential adsorption of ions that follow the Hofmeister series. Finally, the stability of unsaturated fatty acid monolayers towards oxidation will be briefly discussed.

COLL 263

Linker-assisted attachment of quantum dots to TiO_2 through a "one pot" in-situ method and using a novel bifunctional organic linker molecule

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Linker-assisted assembly is an attractive strategy for attaching quantum dots (QDs) to TiO_2 surfaces. This presentation will focus on two approaches to increasing surface coverages of QDs on TiO_2 and improving the reproducibility of linker-assisted assembly. The first involves an *in situ* assembly strategy, in which synthesis of QDs and their attachment to surfaces occur in the same reaction mixture. Bifunctional mercaptoalkylcarboxylates serve both as capping groups and bifunctional linkers, enabling attachment of as-synthesized CdSe QDs to TiO_2. The second approach involves the use of 2-mercaptoethylphosphonic acid (MEPA) as a bifunctional organic linker to tether QDs to TiO_2. MEPA was chosen as an alternative to carboxylated linkers because phosphonic acids have been shown to adhere more strongly to metal-oxide surfaces. MEPA was synthesized from diethyl(2-bromoethyl)phosphonate by reaction with triphenylmethylmercaptan followed by deprotection and deesterification. The attachment of MEPA to TiO_2 and QDs to MEPA-functionalized TiO_2 surfaces will be discussed.

COLL 264

Immobilization and characterization of viscosity-sensitive 9-(2-carboxy-2-cyanovinyl) juolidine (CCVJ) into zirconium phosphonate layers for determination of interfacial viscosity

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Multilayer thin films of zirconium phosphonates and mixed layers of zirconium phosphonates growing from layers of methyl-terminated monolayers have been grown on oxidized silicon and gold surfaces by sequential adsorption. The initial surface layer is either an amine-terminated siloxane or thiol, respectively which is then chemically converted to a phosphonate group. Subsequent exposure to Zr^{4+}

and 1,8-octanediphosphonate yields linear layer-by-layer growth of zirconium 1,8-octanediphosphonate (ZODP) up to 6 layers. The terminal phophonate group can then be chemically converted back to an amine for attachment of a viscosity-sensitive dye, CCVJ. The resulting thin films were characterized by ellipsometry, polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS) and atomic force microscopy (AFM) and fluorescence microscopy. Results from these studies will be presented and the application of these modified surfaces to determine interfacial viscosity in different fluids will be discussed.

COLL 265

Single molecule manipulation of double-decker pthalocyanine molecules using scanning tunneling microscope under ambient conditions

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Precise control over the position and orientation of organic molecules at the nanoscale is critical for the development of molecular-scale devices. Scanning tunneling microscopy (STM) has proven to be an effective tool for manipulating atoms and small molecules at low temperature and under ultra-high vacuum conditions. Here, we demonstrate single molecule manipulation of isolated pthalocyanine-based double-decker molecules on highly ordered pyrolitic graphite (HOPG) using an STM probe tip under ambient conditions. Metal-free pthalocyanine $H_2Pc(OC_8H_{17})_8$ was co-adsorbed with lanthanide sandwich complex molecules $(Pc)Lu[Pc(OC_8H_{17})_8]$ on HOPG at 80 °C, and the surface-adsorbate and adsorbate-adsorbate interactions were studied. We exhibit successful manipulation of isolated double-decker molecules to fabricate features of interest. We explore the role of the structure of the bottom ligand of the double-decker molecules during and after the manipulation process. This manipulation capability paves the way to synthesize and to study novel one-dimensional functional materials for the development of molecular electronics.

COLL 266

Synthesis of ceria nanocrystal with controllable size and shape

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Nanocrystalline cerium oxide (nanoceria) was synthesized in non-polar solvents using high temperature decomposition of various cerium precursors including cerium acetylacetonate hydrate, cerium-oleylamine mixture, and cerium nitrate hexahydrate. Near-spherical cerium oxide nanocrystals were formed readily and their dimensions could be well controlled from 3.5 to 10 nm. It was found that the size of cerium oxide nanoparticles is highly dependent on the concentration of cerium and oleylamine mixture as well as the presence of additives such as water and octadecylamine. Star and flower-shaped nanoceria was also prepared by the reaction of cerium nitrate or cerium acetylacetonate with the same equivalent amount of oleylamine as oleic acid. The Ce(III) concentration in nanoceria varied and was inversely related to particle diameter. Water-soluble nanoceria was further produced via phase transfer using polyacrylic acid octylamine (PAAOA) and oleic acid. Both methods showed high transfer efficiency (over 80%) without change to the nanocrystal size or morphology. The acute toxicity of these nanoceria particles to Human dermal fibroblasts (HDF) was quite minimal, which shows great potential for biomedical applications.

COLL 267

Aging in depletion-induced colloidal gels

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We report a systematic experimental investigation of aging in a model colloidal gel system, in which an attractive depletion interparticle interaction of tunable strength is induced by the addition of a non-adsorbing polymer to an initially stable suspension of density and refractive index-matched PMMA particles. The effects of colloid volume fraction and polymer concentration on aging are investigated in these systems. At high colloid volume fractions, dynamic rheological measurements show a remarkable increase of over several orders of magnitude of the relevant rheological parameters with gel age. However, the behavior is markedly different with dilute gels. The microstructural phenomena that cause this behavior are investigated with quantitative confocal microscopy. Finally, the effects of primary particle geometry on aging are investigated and discussed.

COLL 268

Modified calcium surfaces as optimal tissue scaffolds

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Providing an optimal tissue scaffold is critical for the regrowth of bone at a major injury site. In this study, calcium aluminate (CA) and calcium phosphate (CP) were investigated as potential bone tissue scaffolds. Furthermore, CA and CP were modified with melatonin (N-acetyl-5-methoxytryptamine) in an effort to enhance cell viability and proliferation. Melatonin was attached to the CA and CP surfaces via a two-step reaction and attachment was confirmed using Diffuse Reflectance Infrared Fourier Transform spectroscopy. Cell viability and proliferation of human osteoblasts on these surfaces was measured. Osteoblast viability and proliferation on these surfaces were quantitatively measured at growth points of one, four, and seven days. The data was analyzed using one way ANOVA statistics. The successful immobilization of melatonin improved cell adhesion.

COLL 269

Aggregation kinetics of silver nanoparticles induced by chloride and fluoride ions

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The rate of nanoparticle aggregation in solution increases with ionic strength due to an increase in the screening of the electrostatic repulsion between the particles. Chloride ion is typically used as an aggregation agent in SERS experiments, but, according to the DLVO theory, any salt solution with the same ionic strength should exhibit the same effect. Yet, we find that chloride ion and fluoride ion have very different critical coagulation concentrations – the concentration at which the aggregation rate becomes diffusion-limited. We have measured aggregation rate constants as a function of halide concentration and compared them with those calculated using a pair-potential which combines a van der Waals attractive potential with an electrostatic repulsive potential. This comparison shows that the difference in the two halide ions is likely due to their effect on the nanoparticle surface charge. Details of the experiments and analysis will be presented.

COLL 270

Insights into the sulfur gold interaction through use of a novel precursor

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Sulfur interaction with gold surfaces has attracted interest for numerous technological applications including heterogeneous catalysis, nanotechnology, and corrosion. Deposition of sulfur on metals is typically conducted in aqueous electrolytic solutions using sulfur precursors such as S^{2-}, SH^-, or H_2S, or in gas phase using S_2 or SO_2. We have recently introduced a new sulfur precursor, previously exploited for sulfur donation in organic synthetic chemistry, but never in sulfur on metals deposition. Our results clearly suggest the new precursor efficiently achieves deposition of S on Au, and spontaneous deposition in various organic solvents enables use in novel environments. XPS, STM and electrochemistry show the modification is rapid, within minutes leading to long range ordered domains of rectangular structures resembling those observed under electrolytic aqueous and gas phase conditions. Notably, imaging areas with missing rectangles clearly shows these to be independent, moving as units rather than part of more complex phase structures.

COLL 271

Characterizing surface properties of *Bdellovibrio bacteriovorus* with functionalized AFM probes

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Bdellovibrio bacteriovorus can exist as either a host dependent (HD) predator of a variety of Gram-negative bacteria, or a host independent (HI) bacterium that feeds on extracellular nutrients. AFM analysis of live cells in buffer was used to examine the surface properties of both forms of *Bdellovibrio.* Both HI and HD *Bdellovibrio* were immobilized with polylysine. HI *Bdellovibrio* biofilms were also probed directly. In addition to measuring stiffness, force curves from chemically functionalized ($-(CH_2)_{12}CH_3$ and $-(CH_2)_{12}COOH$) AFM tips were used to evaluate adhesion, hydrophobicity, charge, and the acid/base properties of both HD and HI *Bdellovibrio*. Experiments done on biofilms of HI *Bdellovibrio* demonstrate that the tip-cell adhesion values are a factor of 10 greater when a hydrophilic tip is used instead of a hydrophobic one. Comparisons of adhesion data between HD and HI *Bdellovibrio* as well as the mode of adherence to the sample slide for HI will be discussed.

COLL 272

Liquid metal nanoparticles by molecular dissassembly

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We report the development of simple synthetic route for the preparation of room-temperature liquid metal nanoparticles by exploiting directed self-assembly. Generally, metallic nanoparticles are produced by a carefully controlled reduction of metal salts, but this strategy is untenable for many metals, alloys, and semiconductors. Low-melting metals and alloys based on gallium, indium, and mercury have been used previously as substrates for thiol-based self-assembled monolayers (SAMs). We have adopted an approach where we prepare nanoparticles from these liquid alloys by agitation in the presence of a thiol solution. As the liquid metal separates into particles of decreasing size, SAMs rapidly form on the newly exposed metal surfaces. By designing intermolecular interactions between the adsorbed molecules, strain is induced at the interface to assist the disassembly of these soft metals into spherical particles with a diameter between 5 and 50 nm.

COLL 273

Changes to cell surface chemistry of *Pseudomonas putida* grown on polycyclic aromatic hydrocarbons

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Pseudomonas putida is used in bioremediation applications due to its ability to use various polycyclic aromatic hydrocarbons (PAHs) as carbon sources. Here we use both AFM and chemical characterization of membrane extracts to explore changes in *P. putida* surface chemistry when it is grown on PAHs. AFM imaging demonstrates that *P. putida* biofilms can grow directly on anthracene crystals and cause distinct decreases in anthracene coverage. Cells grown with either anthracene or fluoranthene as their sole carbon source produce a higher molecular weight, amphiphilic, membrane-associated compound that is either not present or minimally present in cells grown on conventional carbon sources (glucose, acetate, rich media). Since we suspect this compound assists cell growth on PAHs, AFM force curves on live *P. putida* cells are currently being collected to assess changes in cell surface hydrophobicity for bacteria grown on PAHs.

COLL 274

Surface modification of Nickel nanofibers via polymer grafting

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The forests of high aspect ratio (magnetic and conductive) nickel nanofibers were manufactured electrochemically using alumina membranes. Next, the polymer brushes were grafted to the surface of the nanofibers using "grafting to" method via surface bound epoxy functionalities. As a result hybrid composite nanofibers with core-sheath morphology have been synthesized. The grafting of polymer brushes was used to bring functionality to the surface of the nanofibers and prevent nanofibers from permanent sticking. Specifically, we functionalized the head and bottom part of the nanofibers with grafting of different polymers. The target was to tune surface behavior of the nanofibers in responce to pH, ionic strength, and temperature change.

COLL 275

Stabilization of soft lipid colloids via nanoparticle decoration and its interplay with supported lipid bilayer formation

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Stabilization against fusion of zwitterionic lipid small unilamellar vesicles (SUVs) by charged nanoparticles is essential to prevent premature inactivation and cargo unloading. In the present work we examined the stabilization of DMPC and DPPC SUVs by monolithic silica (SiO_2) nanoparticle envelopment. We found that for these soft colloids stabilization is critically dependent on whether fusion occurs between the charged nanoparticles and neutral SUVs to form supported lipid bilayers (SLBs), or whether the reverse occurs, namely nanoparticle decoration of the SUVs. While SLB formation is accompanied by precipitation, nanoparticle decoration results in long term stabilization of the SUVs. The fate of the nanosystem depends on the size of the nanoparticles and on the ionic strength of the medium. We found that in the case of highly charged SiO_2 nanoparticles in water, there is no SUV fusion to SiO_2 for a specific range of nanoparticle sizes. Instead, the negatively charged SiO_2 nanoparticles surround

the uncharged SUVs resulting in electrostatic repulsion between the decorated SUVs, thus preventing their aggregation and precipitation. This study has great potential impact towards better understanding the interaction of nanoparticles with biological membranes and the factors affecting their toxicity and their use as drug carriers or sensors.

COLL 276

Reactions of several copper ALD precursors on metal surfaces

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The Atomic Layer Deposition (ALD) method is one of the promising way to deposit conformal copper seed layer on the surfaces of complex interconnect structures. Several copper-organic precursors have shown great promise for the ALD applications, but potentially deposit impurities that may degrade the quality of the seed layer and hinder their practical applications. The goal of our work is to develop a molecular-level understanding of the surface chemistry of those compounds to design more efficient and cleaner copper ALD processes. In this work, three copper precursors, bis[(*N,N'*-di-*sec*-butylacetamidinate)Cu], Copper(N(1(dimethylvinylsiloxy)-1-methylethano)-2-imino-4-pentanoate) (CuKI5) and Copper (II) acetylacetonate were used. Several methods have first being developed to control the dosing of several low-vapor-pressure copper precursors onto metal surfaces inside an ultrahigh vacuum (UHV) chamber in order to control its coverage. The following thermal chemistry of the adsorbates has then been investigated by X-ray Photoelectron Spectroscopy (XPS), Low Energy Ion Scattering (LEIS), Reflection-Absorption IR Spectroscopy (RAISE) and Temperature Programmed Desorption (TPD). The effect of coadsorption of hydrogen has been investigated. Several stages of reactivity have been identified. For example, the bis[(*N,N'*-di-*sec*-butylacetamidinate)Cu] initially decomposed to the ligands and the further conversion of the alkyl moieties in those amidines via beta-hydride elimination steps to produce butene and small amidine. No appreciable changes observed while coadsorpted hydrogen on the surfaces, because the hydrogen desorped before 350 K, which temperature was just high enough for the precursor to react on the surfaces. Coverage and depositting rate of those precursors were also identified by XPS and LEIS. For bis[(*N,N'*-di-*sec*-butylacetamidinate)Cu], 15 L dosing can total covered the surfaces, three cycles of dosing can form one copper monolayer, the average depositing rate is ~0.7Å/cycle.

COLL 277

Investigation of the chemoselective hydrogenation of cinnamaldehyde utilizing a variety of platinum based catalysts

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The chemoselective hydrogenation of carbonyl bonds in unsaturated ketones and aldehydes is a vital reaction in fields ranging from pharmaceuticals to fragrances. The hydrogenation reaction of cinnamaldehyde was investigated utilizing four different types of catalysts: colloidal spherical platinum nanoparticles; colloidal shaped platinum nanoparticles; colloidal intermetallic nanoparticles; and high surface area supported platinum nanoparticles. Each catalyst type was investigated by carrying out a hydrogenation reaction in a bench top pressure reactor, and intermittently, removing and injecting aliquots into a GC/MS instrument. From the chromatogram, peaks were integrated and relative percentages of each component in the reaction system were determined. From this data percent selectivities and turnover frequencies were determined. Also, differential equation modeling techniques were utilized to determine factors about the chemical kinetics of the system. This kinetic data was then used to determine the overall effectiveness of the catalyst. From these conclusions it is possible to determine, at a molecular level, the necessary composition and properties of a truly chemoselective catalyst.

COLL 278

Seeing charges on polymer surfaces: Kelvin force microscopy of charged polymers

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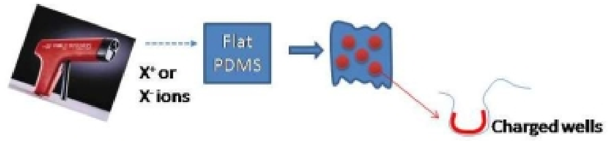
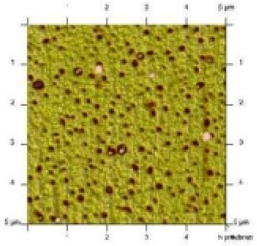
Polymeric (insulator) materials can be charged upon contact to other materials or themselves and store the developed charged for a long time i.e. several hours to days. Although there are numerous studies on charged polymers, it is still unclear how these charges can be preserved for such a long time on the surfaces of these polymers. To investigate this phenomenon we sprayed ions from an “ion-gun” onto the polymers such as PDMS, PC and PMMA and investigated the charge development and decay at macroscopic level and also investigated the changes on the surfaces by Atomic Force Microscopy (AFM)

and Kelvin Force Microscopy (KFM).





Locating and seeing charges on polymeric surfaces is of great help to understand the mechanism of charging on these surfaces which is important not only for the basic scientific research but also for practical purposes such as the prevention of static electricity on the polymer surfaces upon their manufacturing and utilization. Literature and Notes: [1] a) R. G. Horn, D. T. Smith, *Science* **1992**, *256*, 362-364; b) R. G. Horn, D. T. Smith, A. Grabbe, *Nature* **1993**, *366*, 442-443. c) Jacobs, H. O., Whitesides, G. M. *Science* **2001**, *291*, 1763-1766. This work was supported by the US Department of Energy, Office of Basic Energy Sciences as part of the Non-Equilibrium Energy Research Center (NERC), an Energy Frontier Research Center.

COLL 279

Formation and patterning of octadecyl silane monolayers on a silicon substrate via atomic force microscopy

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The controllable creation of nanometer-sized patterns is critical for applications such as biosensing and electronics. In this study, two self-assembled monolayers, octadecyltrichlorosilane (OTS) and octadecyldimethylchlorosilane (ODMS), were formed on a SiO_2/Silicon (100) substrate and characterized through ellipsometry and contact angle measurements. Despite similar structure and bonds to the surface, the methyl groups in ODMS lead to a significantly thinner and less well packed monolayer than that of OTS. Stemming from this difference in packing, atomic force microscopy based patterning of these two layers, under nearly identical conditions, resulted in drastically different patterns. At low applied load, rearrangement, but not removal, of the ODMS monolayer was observed. Interestingly, the behavior of the patterning in the ODMS monolayer depends consistently on the relative humidity under which the patterning was performed. The water from ambient humidity may play a significant role in the etching process and this role is being investigated.

COLL 280

Contact electrification in waterfree media

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Contact electrification (CE) is a phenomenon whereby charge develops on two surfaces that are brought into contact and then separated. CE has long been applied in several useful technologies including photocopying, laser printing, and electrostatic separations, but its mechanism, despite history of research dating back to Thales of Miletus, remains poorly understood. Numerous studies tried to correlate charging with either electron[1] or ion transfer[2] and we and others have also considered the effects of the atmosphere and relative humidity on CE. Up to now, the results have been inconclusive suggesting that depending on relative humidity and the material properties of contacting materials, H_2O contained in air can either promote or inhibit CE mostly because experimental techniques used so far do not completely eliminate water from the atmosphere around the contacting materials. Here we provide a simple yet conclusive water-free environment for contact electrification, under a highly non-polar liquid paraffin oil maintained under dry, inert atmosphere. Water-free conditions are realized by performing all preparations and charge measurements under oil-immersion. Revealing the role of water in contact electrification is important not only for basic understanding about the mechanism of contact electrification but also for applications of charge dissipation i.e. prevention of static electricity in production and utilization of all polymeric products. Literature and Notes: [1] C. Y. Liu, A. J. Bard, *Nat. Mater.* **2008**, *7*, 505-509. [2] L. S. McCarty, G. M.Whitesides, *Angew. Chem*. **2008**, *120*, 2218-2239;*Angew. Chem. Int. Ed*. **2008**, *47*, 2188-2207. This work was supported by the US Department of Energy, Office of Basic Energy Sciences as part of the Non-Equilibrium Energy Research Center (NERC), an Energy Frontier Research Center.

COLL 281

Size and surface dependence of silver dissolution: Toward wider applications of nanoAg antimicrobials

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Silver nanoparticles (nanoAg) have been widely used for antimicrobial applications. But for bactericidal use in water purification applications, nanoAg use is limited by its slow dissolution kinetics. Moreover, tuning the antimicrobial activity and determining the role of particulate/ionic contribution in antibacterial activity is challenging, because of the difficulties associated with the synthesis. In this study, we develop an approach to synthesize organic soluble nanoAg, in the range of 2-15 nm (size distribution <10%). Size tunability was collectively governed by the surfactant-to-metal ratio, reaction temperature and time. Highly crystalline nanoAg was then made water soluble using PEG-thiols for further antimicrobial studies. Dissolution profiles of the aqueous nanoAg were also explored to understand the size dependency on antimicrobial nature, as well as the mechanism of toxicity. Morphology and chemical composition studies were done using TEM, ICP-MS, DLS, FT-IR, UV-Vis, XPS, XRD and EDS.

COLL 282

Physicochemical and interface studies of lignocellulosic model surfaces

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In this work, lignocellulosic model surfaces were obtained and studied. These surfaces are a potential useful tool that allows enzyme-surface interactions studies, in a reproducible and controlled way, to get a better understanding of the controlling factors of such interactions. In order to do this, solutions of microcrystalline cellulose and kraft lignin in tetrahydrofuran (THF) at room temperature were obtained. These solutions were characterized by means of Fourier-Transform Infrared (FTIR) and ultraviolet-visible (UV-vis) spectroscopies. Different biopolimers configurations were observed, possibly due to solubilization conditions. Using these solutions, physicochemical and morphological properties of Langmuir films of cellulose, lignin and their mixtures were studied using surface-pressure vs area per molecule (∏-A) isotherms and Brewster Angle Microscopy (BAM). All of the produced lignocellulosic films presented one condensed phase, did not had collapse, and probably form multilayers. These Langmuir lignocelullosic films showed to be suitable for deposition onto a solid substrate (functionalized silica) using the Langmuir-Schaefer (LS) deposition technique and they were morphologically and topologically characterized by means of Atomic Force Microscopy (AFM). Finally, stability properties of the lignocellulosic model surfaces were studied by means of a Quartz Crystal Microbalance with Dissipation (QCM-D).

COLL 283

Singlet-triplet spin-orbit coupling and crossing probability for the single-dimer cluster model of a Si(100) surface

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The minimum energy crossing point of the singlet to triplet crossing for a single Si-dimer cluster has been determined using a variety of computational techniques. The crossing points located by the various computational methods were similar in structure and close to the triplet state in energy. At the crossing point, the spin-orbit coupling (SOC) coefficient was determined to be approximately 25 cm^{-1}. Small geometry differences at the crossing points located by the different computational methods had insignificant influence on this value. Using this SOC, the Landau-Zener spin-crossing probability at room temperature was computed to be approximately 0.5%. These results will be extended to examining crossing during the decomposition of benzene and chlorobenzene on the Si(100) surface.

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WITHDRAWN

COLL 285

Mechanistic study of the production of silver nanoparticles

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A standard synthesis of silver nanoparticles in aqueous solution relies on the reduction of silver ions by sodium borohydride in the presence of sodium citrate. Nonetheless, the overall reaction has not been unambiguously determined. The focus of the current study is to identify and quantify the reaction products. To this end, we have constructed a mass spectrometer apparatus that allows us to sensitively monitor in real time gas phase species produced during the synthesis of the nanoparticles. One significant difference between some of the reactions that have been proposed in the literature is the production of H_2. We will present our results on the time evolution of H_2 as well as results of isotopic substitution

experiments designed to determine the source of the evolved H_2. We have also used B^{11} NMR to determine what boron species are present in the products.

COLL 286

Organophosphate degrading enzymes bearing metal organic framework for decontamination of chemical warfare agent (CWA)

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QNA-TSG has developed reactive Metal Organic Framework (MOF) materials, by using the MOF as an organophosphate degrading enzyme support and by developing new linker chemistries in the MOF that render the material intrinsically reactive towards CWA agents in air and wet environments. Interestingly, self-decontaminating metal organic framework (SD-MOF)s are stable in wet environments, highly compatible with organophosphorous hydrolase (OPH) enzyme, and can be reused multiple times without affecting efficacy of reactivity, and can be regenerated with a simple rinse (methanol) at ambient conditions. As the entire adsorbent surface of SD-MOF would offer reactivity, the realization of this effort represents a completely new paradigm for designing reactive adsorbents. These new reactive decontaminating materials in conjunction with OPH enzyme, could find application for cartridges for masks, either continuously stirred tank reactors (CSTR) or packed bed reactors (PBR) for waste water management.

COLL 287

Characterization of hydrothermally synthesized zinc oxide (ZnO) nanoparticles

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Zinc oxide (ZnO) is a chemically and thermally stable n-type semiconducting material with extremely high sensitivity to combustible and reducing gases and has therefore been successfully used as a transducer in gas sensing, chemical

and biological, photovoltaic, piezoelectric and fuel cell devices. To optimize ZnO conducting/semi-conducting properties for these applications, we seek to control the size distribution and morphology while fabricating the nanostructures. We have hydrothermally synthesized ZnO nanoparticles at low temperatures, varying the temperature between 40–90°C. A critical morphology change was observed at ca. 60°C. Control of the ratio of rod-like to nanoparticle-like shapes (30–70 nm diam.) along with mean diam., affecting sensing properties, can be achieved via temperature control during the ZnO synthesis.

COLL 288

Surface chemistry of pentakisdimethylamido tantalum on tantalum surfaces

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The surface chemistry of pentakisdimethylamido tantalum (PDMAT), a precursor commonly used for atomic layer deposition (ALD), has been studied on a Ta foil. Temperature-programmed desorption (TPD) results indicate multilayer desorption at 250K and a broad monolayer peak starting at 350K. H_2, CH_4, C_2H_4, and CH_3NCH_2 were identified as the main desorption species. They are also seen in isothermal kinetic data obtained using a molecular beam arrangement above 500K, with yield ratios of 0.67:0.14:0.08:0.08. All C-H bond dissociation, C-N bond dissociation, Ta-N bond dissociation and beta-hydrogen elimination reactions are seen with the amido ligand occur on the Ta surface. Upon ammonia molecules addition, the yields for H_2 and CH_4 decrease and that for dimethyl amine($NH(CH_3)_2$) increase above 550 K. Isotope labeling was used to establish that hydrogenation of the amido groups requires hydrogen atoms from the ammonia.

COLL 289

Synthesis of biocompatible zinc sulfide nanocrystals and their application to phototherapeutic reactions

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The development of semiconductor nanocrystals for utilization as photocatalytic materials is of particular interest because of potential uses in photodynamic therapy. In order for these materials to be utilized, their properties must be well-understood. Our present work deals with the synthesis, characterization, and photocatalytic activity of zinc sulfide nanocrystals that are capped by amino acids. Photoreactions have been carried out on bilirubin, a compound important in understanding jaundice in newborns. Initial photoconversion experiments, conducted in the absence of and in the presence of amino acid-capped nanocrystals, indicate that the ZnS nanocrystals enhance the rate of bilirubin photoconversion. Reactions carried out after bubbling nitrogen through the solutions suggest that under aerobic conditions the mechanism operates through a singlet oxygen pathway, while under anaerobic conditions photoconversion still takes place, but through a mechanism involving photoisomers. Taken together, these results provide preliminary evidence that these nanocrystals may be suitable for phototherapeutic applications.

COLL 290

Simulating nanoparticles and surfactant in the vicinity of oil/water interfaces

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Understanding the mutual behavior of surfactants and nanoparticles in oil/water systems remains an outstanding problem. Nanoparticles and surfactants are each known to stabilize the oil/water interface through different mechanisms. The increasing prevalence of nanoparticles in industry and commercial products involving surfactants, oil and water results in a pressing need to study and characterize these systems. Here we present coarse grained molecular dynamics simulations of nanoparticles and surfactants in the vicinity of oil/water interfaces. Computer simulations offer an inherently high spatial resolution and control of composition and conditions, which enables us to prepare systems of varying surfactant and nanoparticle concentration. Using statistical mechanics we are also able to evaluate thermodynamic properties and free energies which give valuable insight into the rich behavior of these systems, which may be useful both for a fundamental understanding and for designing systems for novel applications.

COLL 291

Measuring the intracellular stability of monolayer-protected CdSe quantum dots using laser desorption/ionization mass spectrometry (LDI-MS)

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Cadmium selenide (CdSe) quantum dots have promising applications in renewable energy due to their luminescence and photo-stability. However, they pose an environmental hazard due to the Cd2+ ion contained within the quantum dot. The focus of this research is to develop a ligand to stabilize the CdSe quantum dot in biogenic solutions, thereby reducing potential toxicity. The CdSe quantum dots are functionalized by attaching monothiol and dithiol ligands to their outer zinc sulfide shells and subsequently attaching one of four different functional groups to the ends of the ligands, followed by placing each CdSe-ligand pair in different biogenic target solutions. The amount of surface ligands displaced by biogenic thiols is quantified using LDI-MS after 24 hours. The results suggest the validity of our hypothesis that a monothiol ligand will better stabilize the quantum dot. Further experiment is needed to completely prove the hypothesis.

COLL 292

High order desorption kinetics of deuterium from the saturated monodeuteride phase of Si(100)

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The thermal desorption of hydrogen from the monohydride phase of Si(100) is among the best known and studied reactions in surface science. Most kinetic studies have focused on the moderate (0.1 to 0.5 ML) and low (<0.1 ML) coverage regimes, for which desorption is 1st order and 2nd order in the H atom concentration, respectively. In the current study, we use angularly-resolved isothermal desorption measurements to show that for coverages above 0.8 ML, the desorption becomes 2nd order and perhaps even higher. Because the activation energy and angular distribution are similar to those in the moderate coverage regime, we can rule out any possible contributions from the dihydride desorption. The results will be discussed in terms of the 2H/3H/4H model. Experiments were performed in an ultrahigh vacuum apparatus having a doubly differentially pumped mass spectrometer and modulated detected flux.

COLL 293

Study on the spectral evolution of oligonucleotide-functionalized gold nanoparticle agglomeration - toward quantitative DNA colorimetric detection

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Gold nanoparticles scatter visible light strongly because they support localized surface plasmon resonance. The aggregation of gold nanoparticles induces the scattering color change which is manifested as a shift in extinction peak positions and a broadening of peak widths. This phenomenon has been exploited to detect DNA using oligonucleotide-functionalized gold nanoparticles in the past. We investigated DNA-induced spectral change of nanoparticle dispersion in order to estimate the concentration of target DNA strands. Oligonucleotide-functionalized gold nanoparticles were mixed with various concentrations of target DNA. The resulting change in peak shifts and peak width of nanoparticles with different sizes and oligonucleotide surface densities was measured and analyzed. Our results indicate that an optimum target DNA-to-nanoparticle ratio exists where the peak shift and peak broadening are maximized. Kinetic studies of nanoparticle aggregation leading to surface plasmon shifts will also be presented.

COLL 294

Nucleic acid sample preparation: Reversible interaction between DNA and surfaces

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The reversible interaction of DNA and RNA with silica surfaces enables solid phase extraction of nucleic acids from complex clinical samples. To further our understanding of these reversible interactions, we are quantifying the adsorption/desorption of DNA to/from microparticles as function of particle composition (silica particles versus silica-zirconia composites), surface modification, composition of the binding buffer (chaotropic versus non-chaotropic, concentration and type of cations), buffer pH, agitation rate (to understand reaction- versus diffusion-limited kinetics), DNA type (plasmid versus linear) and molecular weight (fragmented versus genomic DNA), as well as the influence of contaminants such as proteins and lipids. We are quantifying DNA adsorption and elution via UV/Vis absorbance and PicoGreen fluorescence. DNA elution is further studied via qPCR. DNA adsorption to a quartz crystal surface is characterized via QCM-D. The results of our investigation are applied to the development of novel approaches for nucleic acid sample preparation.

COLL 295

Biomimicry: Investigating solid supported cell membrane models

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Lipid membranes are essential for cellular function, acting both as a selective barrier between the cell interior and its environment as an interface for cell signaling responses and cell communication. Creating model membranes allow for the complexities of membranes to be characterized in hopes of furthering the understanding of lipid membrane function and physiology. In this research, we have used acoustic and optical techniques to study a self-assembling membrane system. Our study of membranes focuses on the interactions between the lipid membrane and the support on which it is formed, as well as the factors that govern the self assembling mechanism. Specifically, osmotic pressure contributes to lipid-support interaction. By varying the osmotic potential, we can facilitate the membrane formation process.

COLL 296

Preparation of gold nanoparticles using sodium alginate as a stabilizer

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Gold nanoparticles were synthesized by reduction reaction of tetrachloroauric acid using sodium borohydride as a reducing agent and sodium alginate as a stabilizer at various concentrations. Analysis by transmission electron microscope revealed that average size of gold nanoparticles was 5 nm and better distribution of gold nanoparticles in the solution was achieved with increasing the concentration of the stabilizer. After characterization by UV-Visible spectrophotometer, it was found that the wavelengths at maximum absorbance of gold nanoparticle solutions synthesized with and without the stabilizer were at 511 nm and 521 nm, respectively. As the concentration of the stabilizer increased, the absorbance intensity decreased.

COLL 297

Amphiphilic polymer vesicles migration towards water/oil interfaces

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We have found synthetic polymer vesicles are able to migrate to the common oil/water interfaces. This migration is due to the surface charges of vesicles, which results in an autonomous motion to the interface. We further utilize this phenomenon to deliver cargo (dye) to the oil phase by the disassociation of vesicles.

COLL 298

Functionalized gold nanoshell for the delivery of biological therapeutics to the macula

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Gold nanoshell continues to attract attention for researchers due to its unique biomedical application in photothermal therapy. In this presentation, gold nanoshells functionalized with poly(ethylene glycol) was employed to use in a novel paradigm of biologically photothermal therapy. Functionalized gold nanoshells are covalently attached to the desire antibodies or drug molecules via photothermally labile linker, which can recognize target cells specifically. Once accumulated, near IR laser light was illuminated to cause the efficient local heating, thereby destroying target cells.

COLL 299

Surface modification of metallic nanoparticles for effective destruction of brain tumor cells

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Synthetic procedures that produce nanoscale materials with controlled morphology are advantageous particularly when utilizing nanomaterials for biological applications. We have developed a strategy to fabricate metallic nanoparticles and examined their toxicity toward brain tumor cells. Non-toxic

nanoparticles were used as scaffolds to conjugate stilbene derivatives. Neither the stilbene molecules nor the metallic nanoparticles showed any activity on their own toward brain tumor cancer cells. However, when the stilbenes were conjugated onto the nanoparticle surface, the resulting hybrid was highly effective in killing the cells. We attribute the effect to polyvalent interactions between the stilbenes and the cells when bound to the nanoparticle surface. Furthermore, we have investigated the effects of surface binding on the activity of stilbene derivatives and correlate surface morphology to activity. The presentation will focus on the synthesis and characterization of the nanoparticles, attachment of the stilbenes and their interactions with brain tumor cells.

COLL 300

Surface chemistry of aromatic nitriles on Cu(111): From hydrogen-bonded to coordination networks

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Deposition of 9,10-anthracenedicarbonitrile (DCA) onto a Cu(111) surface leads to the formation of a nearly-square hydrogen-bonded adsorbate pattern, which by annealing to room temperature can be titrated gradually with substrate atoms thermally released from step edges. Ultimately, this leads to the formation of a hexagonal network, in which each nitrile group coordinates a copper atom, as visualized by STM. Further analysis of the charge density distribution indicates that the Cu adatoms have anionic character, i.e. they are capable of donating electrons to DCA ligands without becoming partially positively charged. Using 3-phenyl-2-propynenitrile, we find large pinwheel structures on Cu(111) which emerge from a smaller, commensurate hexagonal structure.

COLL 301

Synthesis and characterization of Pt and Pt-Cu nanoparticles with selective size and shape for further catalytical applications

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The design and controlled fabrication of nanoscaled materials for catalytical applications have gained a lot of interest in the last decade. It has been

demonstrated that metallic nanoparticles behave differently from the ill-defined catalysts. Moreover, the presence of a second metal may improve these novel features found only in nanoparticles. Here we show the results obtained from an undergraduate senior project in which the synthesis of colloidal Pt and Pt-Cu nanoparticles was carried out by different methods. These metals were chosen to be studied due to their applicability in hydrogenation reactions. The synthesis methods for both the mono and bimetallic systems involved the use of ethanol or ethylene glycol as a solvent, hydrogen (only in the ethanolic solutions) to reduce the metals, and PVP as the capping agent. The formation of the nanoparticles was analyzed with both UV-Vis spectroscopy and Transmission Electron Microscopy. Our results show a dependence of the size and shape of the nanoparticles on the concentration ratios between the metals, and between the metals and the polymer. Further studies will involve the study of the catalytic properties of these systems.

COLL 302

Photocatalytic degradation of 4-chlorophenol by Au/Sol-gel TiO_2, Ag/Sol-gel TiO_2, and Au-Ag/Sol-gel TiO_2

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Photoctalytic degradation of 4-Chlorophenol (4-CP) was studied using TiO_2, Au/TiO_2, Ag/TiO_2 and Au-Ag/TiO_2 prepared by the sol-gel methods and commercial TiO_2 (Degussa P25) as photocatalysts. Experiments were carried out in a batch reactor with both catalyst suspended in the solution under an 11 W low pressure mercury lamp of 200-280 nm wavelength. Qualitative analysis of solution was obtained by means of a high performance liquid chromatograph and a total organic carbon (TOC) analyzer. The results show that, with TiO_2 (sol-gel), a decrease in the 4-CP concentration was much faster than that with TiO_2 (Degussa P25). In contrast, the reduction rate of TOC with TiO_2 (Degussa P25) was much higher than that with TiO_2 (sol-gel). The addition of a small amount of either Au or Ag into TiO_2 (sol-gel) significantly improved the catalytic activity but the addition 0.1% Au into 0.1% Ag/TiO_2 did not show any improvement of the catalytic activity.

COLL 303

New, simple method to synthesize lead telluride (PbTe) nanocrystals

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A new, simple method to synthesize lead telluride (PbTe) nanocrystals (NCs) is reported here. $PbCl_2$ complexed with oleylamine was used as lead precursor. Te powders dissolved in TOP (trioctylphosphine) were used as Te precursor. The size and shape of the PbTe nanocrystals were tuned by changing variables such as injection temperature, reaction temperature, reaction time, lead to capping agent ratios, and lead to Te ratio to obtain the best synthetic conditions. The shapes of the PbTe nanocrystals were either spherical or cubic.

COLL 304

Nanoparticle-filled polymer composites with enhanced thermal conductivity

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Thermal management is a required “green” phenomenon to control in materials if improved energy efficiency is to be achieved. Thermal insulation takes advantage of inclusion of regions of low thermal conductivity trapped in the matrix while thermal transport involves adding filler with high thermal conductivity. Metallic and non-metallic fillers in various particle sizes and morphologies are available for use in advancing the technology. Composites based on rubber have notoriously low thermal conductivity. The information presented in this poster captions how the authors have filled both silicone and fluoroelasteomer resins with particles, cured the resins to the rubber state, and measured their thermal properties. The enhanced conductivities have application in fuser rollers common in copy/print technology.

COLL 305

Long-term efficacy of encapsulated ClO_2 antimicrobial coating

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This work investigates the long-term performance of polymer-encapsulated ClO_2 with $ZnCl_2$ as a general surface, antimicrobial coating with “release-killing”, “contact-killing” and “anti-adhesion” properties. Laboratory test shows that the new antimicrobial coating is effective against the bacteria including *B. subtilis, S. aureus, P. aeruginosa* and *E. coli* as well as drug-resistant bacteria. Three log (i.e., 99.9 %) reduction of viable bacteria was obtain within 1 minute contact. Field tests were conducted to study the performance of the antimicrobial coating. The test was carried out in the university computer classroom and involves 140 computers over a period of 14 days during which the classroom has 24 hour access. Each computer had an average of 23 users and accumulated login time of 12 h over a 24 hour period. Results show that computer mice coated with the antimicrobial coating has 80-90 % less bacteria than the control samples over four days of observation.

COLL 306

Multilevel antimicrobial coating for a healthy environment

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This work reports a new multi-level antimicrobial coating with “release-killing”, “contact-killing” and “anti-adhesion” properties prepared from polymer-encapsulated ClO_2, water-in-oil-in-water double emulsion. A slow sustained release of gaseous ClO_2 at a rate sufficient to inhibit bacteria growth was demonstrated for a prolonged period of time (i.e., 28 days). Touch and infectious droplets triggered an increased release of the biocides at the sites of contamination. $ZnCl_2$ (i.e., 30 ppm) was added to provide “contact-killing” properties, while the bacteria adhesion was prevented by the Pluronic polymer used to encapsulate ClO_2. The new antimicrobial coating is effective against the bacteria including *B. subtilis, S. aureus* and *E. coli.* A greater than 5 log (i.e., ≥99.999 %) reduction of viable bacteria was obtained at a short contact time of

ten minutes. Test was also performed for the H1N1 virus and 99 % reduction was observed after 3 min contact with the treated surface.

COLL 307

Coverage, binding, and electron injection rates of thiol vs. amine bifunctional linkers on CdSe solar cells

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Excited state interfacial electron transfer reaction at the quantum dot-linker-substrate interface has implications to affect solar energy conversion of quantum dot solar cells. Three common carboxythiol linkers were used in an electron transfer rates comparison study to two carboxyamine ligands utilizing steady-state and time-resolved picoseconds luminescence spectroscopy. These linkers assisted in the binding of three different size CdSe quantum dots onto TiO2 thin film surfaces. In all cases, the carboxyamine ligands were found to facilitate fast electron transfer injection reactions on the hundreds of picoseconds scale, 10% faster than carboxythiol-assisted electron transfer reactions.

COLL 308

Application of silver nanoprisms for surface enhanced fluorescence

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Silver nanoprisms of varying dimensions were synthesized by chemically reducing silver nitrate and using potassium bromide to control growth. Characterization of silver nanoprisms was performed using UV-visible spectrophotometry and transmission electron microscopy. The nanoprisms were covalently attached to microscope slides and gold mirrors. The preliminary study of silver nanoprisms was performed to investigate the potential for optimal surface enhanced fluorescence application.

COLL 309

Oxidation of gold nanoparticles by Au(III) in polar solvent

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Here, we demonstrate the stoichiometric oxidation of gold nanoparticles by tetraalkylammonium and tetraalkylphosphonium Au(III) complexes in polar solvent. This reaction proceeds according to a conproportionation mechanism generating stable Au(I) complexes of these cations. It is studied for several nanoparticle systems (including thiolate-stabilized particles of different sizes) employing different cations and halides in the oxidant complex. It is shown to be a valuable new tool for the purification and sculpting of Au nanoparticles in organic solvent.

COLL 310

Hydrothermal synthesis of organic-inorganic hybridized cubic nanoassemblies comprising octahedral CeO_2 nanocrystals and hexanedioic acid

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We report the synthesis of cubic nanoassemblies of octahedral CeO_2 nanocrystals in the presence of hexanedioic acid ($HOOC(CH_2)_4COOH$). The products synthesized with hexanedioic acid had a cubic shape with rugged surfaces. In contrast, the products synthesized without hexanedioic acid were octahedral with smooth surfaces. Both products had an average size of 50~80 nm. A high-resolution TEM image of the cubic products showed that the cubic products were composed of smaller primary octahedral nanocrystals with an average size of ~7 nm. In addition, the TEM images suggested that the primary octahedral nanocrystals assembled together in an oriented fashion. These results suggest that the small primary octahedral CeO_2 nanocrystals assembled in an arranged manner to produce cubic nanoassemblies in the presence of hexanedioic acid. Hexanedioic acid possibly bound the primary CeO_2 octahedral nanocrystals during hydrothermal synthesis of CeO_2 and realized their ordered assembly.

COLL 311

Homologous series of surface structures on $SrTiO_3$ (110)

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All reactions in heterogeneous catalysis occur at the catalyst surface, and active sites are determined by the structure, polyhedral coordination, and metal valence of the surface. Yet such things are poorly understood, limiting our understanding of reaction mechanisms. We have developed methods to crystallographically solve surface structures, and apply them to the surfaces of model catalysts, thereby gaining an understanding on the atomic scale of the mechanisms by which catalysis occurs. Under oxygen rich annealing conditions, the (110) surface of $SrTiO_3$ reconstructs into a homologous series of surface structures with (nx1) periodicity (n=3,4,5,6). Using direct methods analysis of transmission electron diffraction and DFT calculations we have solved these structures, which consist of rings of corner-shared TiO_4 tetrahedra. This has lead to an increased understanding of the forces governing surface structure formation and of the importance of chemical bonding in surface structure stability.

COLL 312

Dimers of Ag nanospheres for surface-enhanced Raman scattering

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There has been a renewed interest in surface-enhanced Raman scattering (SERS) due to its application in ultrasensitive trace analysis and single-molecule detection. It has been shown that the hot spot, or the gap region of a pair of strongly coupled Ag (or Au) nanoparticles, can provide an SERS enhancement factor several orders in magnitude greater than those of individual nanoparticles. Therefore, there is a strong interest to assemble two Ag (or Au) nanoparticles into a dimer with a controllable gap between them. We have successfully developed two methods for the synthesis of well-defined dimers of Ag nanospheres with a range of sizes from 30 to 80 nm, which allows for a systematic study of the hot-spot phenomenon in SERS. The first method was based upon the polyol synthesis, in which growth and dimerization of Ag nanospheres can be accomplished at the same time by adding a small amount of NaCl into the reaction solution. The second method was based upon etching Ag nanocubes with $Fe(NO_3)_3$ in ethanol with the assistance of poly(vinyl pyrrolidone) (PVP). During the etching process, the corners and edges of the Ag nanocubes were truncated off to generate spherical particles, accompanied by dimerization as a result of reduction in colloidal stability due to the addition of ionic species. We further measured the SERS enhancement factors for individual dimers consisting of Ag spheres 30, 40, 63, and 80 nm in diameter, and a value as high as 1.7e+8 was obtained for the dimer made of 80-nm spheres. These new dimers consisting of Ag nanospheres hold great promise in ultrasensitive and single-molecule detection by SERS and are expected to find a range of applications in fields such as surface plasmonics, chemical and biological sensing, and imaging contrast enhancement.

COLL 313

Developing slow flow systems for monitoring initial stages of biofilm formation on microbiologically induced corrosion

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The initial stages of microbe attachment and interaction with metal surfaces serve as a precursor to microbiologically influenced corrosion (MIC). Biofilms. MIC is one of the worst forms of corrosion for metals, and it is often most difficult to identify and correct. This study intends to monitor the initiation and early stages of biofilm formation and MIC and to establish correlations of behaviors with microbial activities. Various flow chamber systems were developed to allow the *in situ* monitoring of biofilm development and its influences on corrosion. The flow systems permit well controlled, low-shear flow conditions commonly encountered in natural MIC environments. In these initial studies, aluminum films, aluminum coupons and carbon steel coupons were utilized, along with two common biofilm bacterial strains, *Pseudomonas aeruginosa* PAO1 and *Escherichia coli*. Some preliminary correlations on biofilm development and MIC behaviors were obtained from the data corrected using these slow flow systems.

COLL 314

Seeding effect on the transformation of $VO(H_2PO_4)_2$ into catalyst precursors $VOHPO_4{\cdot}0.5H_2O$

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Vanadium phosphate hemihydrate ($VOHPO_4 \cdot 0.5H_2O$) with a distinctive morphology has been synthesized in the presence of vanadium phosphate seeds. The reduction of $VOPO_4 \cdot 2H_2O$ with 3-octanol has previously been shown to form $VO(H_2PO_4)_2$. Adding a small amount of $VOHPO_4 \cdot 0.5H_2O$ seed to the reaction mixture changed the product to $VOHPO_4 \cdot 0.5H_2O$ with a distinctive morphology. Studying the reaction with time showed that $VO(H_2PO_4)_2$ was formed initially and could be transformed to $VOHPO_4 \cdot 0.5H_2O$. When the materials were tested as catalysts for butane oxidation the catalyst derived from $VOHPO_4 \cdot 0.5H_2O$ prepared with seeds was found to be highly selective for maleic anhydride compared to $VO(H_2PO_4)_2$ which was found to have very low selectivity to maleic anhydride. This procedure can minimize the amount of $VO(H_2PO_4)_2$ in the catalyst precursor which is known to be detrimental to the catalyst performance.

COLL 315

Peptide fuctionalized metal and quantum dot nanossemblies for mammalian cell imaging and delivery

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The development of multifunctional nanoparticulate vectors for drug delivery into cells has become a coercive tool for therapeutics as well as for understanding the implications of cellular mechanisms. In this work we have functionalized gold or silver nanoparticles with specific peptide sequences such as antigiogenic peptides like adamtsostatin or peptide hormones such as amylin or atrial natriuretic hormone and the crustacean cardioactive peptide. In some cases the peptides were functionalized with quantum dots such as CdSe or ZnS to render the peptide conjugates efficient for bioimaging. The effects of the binding of the nanoparticles on the secondary structures of the peptides was examined by circular dichroism as well as FTIR spectroscopy. The extracellular and intracellular distributions of the conjugates was examined by confocal microscopy in the presence of NRK cells. In some cases, the sizes of the nanoparticles was varied to examine the effects on the assembly of the peptides.

COLL 316

Conformation of yeast cytochrome *c* coated to different sizes of gold nanoparticles under the effect of pH

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The uses of protein-coated metallic nanoparticles including gold as potential colorimetric biosensors and drug delivery vehicles have been studied extensively. A potential biosensor application for detecting protein folding/unfolding is the cytochrome c-coated gold nanoparticles. It was reported (Chah *et al*., Chem. Biol., 12, 323-328, 2005) cytochrome c-coated gold nanoparticles can be potentially used as a colorimetric biosensor for detecting acid-induced folding/unfolding of cytochrome c, based on the observation that upon changes in pH from neutral to acidic, the color of a cytochrome c-coated gold nanoparticle suspension changes from red to blue and to clear. In the present study we comparatively analyzed the secondary structures of cytochrome c coated on gold nanoparticles 13 nm diameter and 19nm and in solution, and their unfolding at various pH conditions by FT-IR spectroscopy. The results of secondary structural analysis revealed that although the color changes coincided with the pH decreases, as reported previously by, this event is unrelated to the true acid-induced unfolding of the protein. The binding of cytochrome *c* to gold nanoparticles induces partial unfolding of the protein event under neutral pH condition. However, the unfolding of the protein does worsen as the pH decreases, the color changes are more related to the changes in sizes of gold nanoparticles than the acid-induced unfolding. By inserting a short linker molecule HOOC(CH2)2S between cytochrome c and gold nanoparticles, 13 nm, the secondary structure of cytochrome c remains native.

COLL 317

Physiological impact of metal oxide nanoparticles in soil-grown *Clarkia* (Onagraceae)

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Despite growing concerns about the potential adverse effects of nanomaterials on the environment, there are no known reports on studies of how soil-borne nanoparticles can affect plants. Given that plants are autotrophs at the base of the food chain, it is critical to understand whether the presence of man-made nanoparticles in the environment can affect plant performance and/or generate cascading effects on their pollinators or herbivores. In this study, three species of the genus *Clarkia* are grown in soil and watered with metal oxide nanoparticles

suspensions of varying concentrations. Tissue and soil samples are taken at regular intervals and nanoparticle concentration are measured using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Growth measurements are also collected at these sampling intervals. Little or no uptake of any nanoparticles was seen. However, stunted growth and chlorosis were seen in unfertilized treatments, suggesting the nanoparticles may affect nutrient uptake through an undetermined mechanism.

COLL 318

Novel hydrogel microspheres with large-scale tunable photonic bandgap

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Environmental stimuli-responsive hydrogel materials have been extensively studied over the last several years because of their potential application in numerous fields. In this report, we have successfully prepared novel monodispersed hydrogel microspheres of poly(styrene-*co*-N,N-dimethylacrylamide) [P(St-*co*-DMAA)] with large-scale tunable (400nm plus) photonic bandgap, rapid response and good redispersibility. This accumulation of P(St-*co*-DMAA) MPs exhibits brilliant structural colors in visible light region that can be observed easily by the naked eye. Moreover, it could extend to near-infrared region. Diffraction wavelength rapid responding to environment variations offers quickly synchronized signals, and thus the material has a potential application as a sensor.

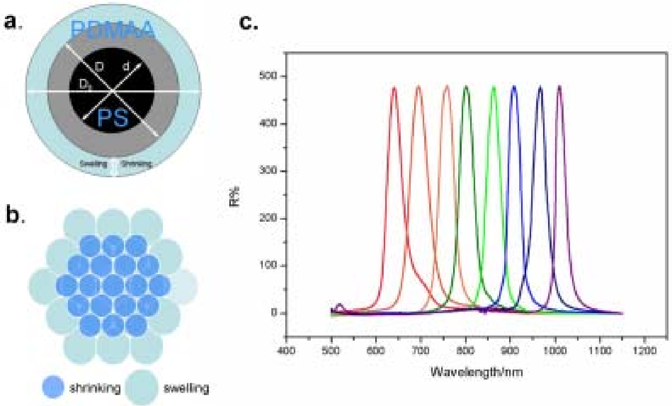

Figure1. (a)Schematic representation for the tunable hydrodynamic diameter of P(St-co-DMAA) MPs with swelling and shrinking. (b)Schematic representation of self-assembled P(St-co-DMAA) MPs in the swelling or shrinking states after centrifugation. (c)Reflection spectra of P(St-co-DMAA) MPs with 0.005 g SDS.

COLL 319

Adsorption of VOCs by activated carbon in the presence and absence of Fe_2O_3 NPs and humic acid

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Adsorption isotherm and column breakthrough experiments evaluating trichloroethylene (TCE) adsorption onto granular activated carbon (GAC) were conducted in the presence and absence of Fe_2O_3 nanoparticles (NPs) and Humic Acid (HA). The zeta potential of Fe_2O_3 NPs was analyzed in the presence and absence of HA. Particle size distribution (PSD) of the NPs dispersions was analyzed as a function of time to evaluate the extent of aggregation. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) analyses were conducted to study the fate and transport of the Fe_2O_3 NPs. Equilibrium isotherm studies have shown no significant effect of the presence of NPs on the adsorption of TCE in the absence of HA. While the presence of Fe_2O_3 NPs and HA decreased the amount of TCE adsorbed in the column breakthrough studies implying competitive inhibition through pores blockage. The zeta potential, concentration, and PSD of NPs were key parameters for TCE removal.

COLL 320

Deposition and transport of engineered metal nanoparticles on silica as a function of environmental conditions

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Increasing use of nanomaterials such as nanozero valent iron (NZVI), Au and Ag in commercial products has led to widespread concerns about their potential environmental and health impacts. To better understand the transport, fate and behavior of nanoparticles in aquatic systems, it is essential to understand their interactions with different components of natural waters including natural organic matter over a broad range of physicochemical conditions on important biogeochemical surfaces such as silica. Nanoparticle sizes are determined by dynamic light scattering. Thin layer chromatography (TLC) is used to characterize the transport properties of nanoparticles on silica while deposition of the nanoparticles onto a silica surface are measured using a quartz crystal microbalance with dissipation (QCM-D), both under similar pH and ionic strength

conditions. We will discuss the connections between the mobility and deposition behaviors of nanoparticles based on these two characterization techniques.

COLL 321

Quantum sized gold clusters for the detection of nerve gas mimics

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In this ever-changing world of science, nanoscale material is at the forefront of research for applications as sensors and catalysts. There has and always will be a need to develop improved methods for the detection of highly toxic organophosphonates and pesticides which mimic the behavior of chemical warfare agents such as Sarin and Tabun. They are highly volatile and react by inhibiting the function of acetylcholinesterase, which shuts down nerve function. We have synthesized and characterized novel quantum sized gold clusters ranging from 1 to 2 nm using 6-(ferrocenyl) hexanethiol and mercaptocoumarin as capping agents. We will present their sensitivity to nerve gas mimics such as diethylchlorophosphate (DCP),malathion, parathion, etc., via fluorescence and electrochemical measurements.

COLL 322

Catalyst deposition in nanostructured smectite clays

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The use of platinum as a catalyst in polymer electrolyte membrane fuel cell (PEMFC) systems has been a cost prohibitive expense in their large scale manufacturing. Maximizing the utilization of platinum catalyst by the incorporation of electronic and ionic conductivity at the reaction interface can reduce the required amount of catalyst for low temperature fuel cells. Catalyst deposition methods using metal salts as a means for cation exchange followed by reduction have been carried out in order to incorporate catalyst sites within the nanostructure of ionically conductive phyllosilicate smectite clays, specifically Laponite® and montmorillonite. Physicochemical properties of the catalyst deposited clays have been determined by extensive characterization including thermal methods, X-ray diffraction, electrochemical impedance spectroscopy, and scanning electron microscopy with energy dispersive X-Ray spectrometry. These analyses reflect the effectiveness of the catalyst deposition process and

provide further insight into optimizing the use of catalyst in PEMFC electrodes using smectite clays.

COLL 323

Optical properties of indium, tin, and gallium doped CdSe quantum dots

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Doping quantum dots to increase conductivity will make it possible for a new generation of electronic devices that are smaller and more powerful than those available today. Elements such as indium, tin, and gallium create electron donor levels that can be thermally or photo-excited into the conduction band. *In-situ* monitoring of photoluminescence from CdSe quantum dots shows the presence of dopant atoms significantly alters the growth kinetics in the heterogeneous size regime. Dopant atoms accelerate the consumption of a magic-sized nano-cluster to provide monomers for growth of a larger quantum dot species. Our studies show that doping has a strong quenching effect on the photoluminescence as a function of temperature. Studies on the effects of ZnS shell thickness suggest that as the shell becomes thicker, gallium migrates from the CdSe host lattice into the ZnS lattice where lattice strain is minimized by a better dopant-host atomic size matching. Our preliminary studies of thin films of doped quantum dots show that doping with indium or tin increases conductivity.

COLL 324

Cyclic voltammetry and the exploration of Gratzel cell electronics

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Solid-State Dye-Sensitized Solar Cells (DSSCs) offer the promise of high-efficiency, low-cost solar conversion. They use a TiO_2 nanostructure populated with photoactive dye to generate excitons and transport negative charge quickly to the anode, while the remaining positive charge is then transported to the cathode via a solid hole transport material. In this paper we use the conjugated polyelectrolyte MPS-PPV. Because of the relative nascence of this technology, the origins of the output photovoltage are still debated in the literature. In this paper we attempt to correlate changes in individual components of DSSCs to changes in the photovoltage, and thus gain information on each component's contribution to the photovoltage. We first modify the electronics of MPS-PPV by introducing it to varying concentrations of the surfactant CTAB. Previous work in

our lab has shown that surfactants bind to polyelectrolytes and change their electronic structures as a function of surfactant concentration. We then use cyclic voltammetry to measure the changes in HOMO level of MPS-PPV. DSSCs are constructed using MPS-PPV in varying surfactant concentrations, and the resulting photovoltages are measured. We then compare changes in the photovoltage with changes to the MPS-PPV HOMO level. From this data, we gain information on the role of the hole-transport material in the entire system. As well, by repeating these experiments using ZnO instead of TiO_2, two different Ru-based dyes, and ITO electrodes instead of SnO, we can make observations on the contribution of each component to the total photovoltage. This will allow future researchers to better control the power output of DSSCs. In addition, by using surfactant to modulate MPS-PPV, we observe an increase in output photovoltage and photocurrent. We thus introduce a novel method for increasing DSSC efficiency using a nontoxic organic material.

COLL 325

Controlled biodegradation of poly(*ε*-caprolactone) using nanoparticles

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Biodegradable poly(*ε*-caprolactone) (*PCL*) / layered silicates nanocomposites have been prepared via solution route. The nanostructures, as observed from wide-angle *X*-ray diffraction and transmission electron microscopy, indicate intercalated and partially exfoliated hybrids depending on the nature of organic modification in nanoclay. The nanohybrids show significant improvement in thermal and mechanical properties as compared to the neat polymer. All the nanoparticles act as nucleating agent and thereby control the crystallite dimension of the matrix. Crystallite dimension of nanocomposites is smaller as compared to pristine polymer. The nature of interaction between different types of nanoclays and *PCL* is verified from enthalpy of fusion and interaction parameters. Biodegradability of pure *PCL* and its nanocomposites have been studied under controlled conditions in enzymes, pure microorganisms (fungi), compost, and alkaline buffer solution. The rate of biodegradation of *PCL* has enhanced dramatically in nanohybrids and depends strongly on the media used. Scanning confocal, electron and atomic force microscopes have used to demarcate the nature of biodegradation of pristine *PCL* and its nanocomposites. The change in biodegradation is rationalized in terms of the crystallization behavior and organic modification in nanoclays of the nanohybrids vis-á-vis the neat polymer. A biodegradation mechanism has been revealed for *PCL* and its nanocomposites through enzyme activity in varying environment. Biocompatibility of the nanohybrid has also been verified.

COLL 326

Flexible worm like micelles from poly(ethylene oxide)-*block*-poly (ε-caprolactone) block copolymers for the aerosolized delivery of agrochemicals

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The aim of this study was to investigate the spray ability of poly (ethylene oxide-*block*-poly (ε-caprolactone) (PEO-*b*-PCL) block copolymer worm micelles and assess their potential application for the solubilization and controlled delivery of agrochemicals to the plants. Flexible worm micelles (contour length, ~15 μm) from PEO-*b*-PCL block copolymer labeled with fluorescent dye, PKH26 were sprayed using an agricultural back pack sprayer and analyzed by fluorescent microscopy for worm contour length. The worms demonstrated survival after spraying on both glass slides and plant leaves but fragmented into shorter worms (lengths, 3-7 μm). Again, sprayed worms demonstrated further survival on drying and rehydration on leaves. A hydrophobic pesticide, Bifenthrin was solubilized by PEO-*b*-PCL worm micelles successfully (~1000 times increase in water solubility) with a loading level of 5% (w/w). In biological study, Bifenthrin loaded worm micelles demonstrated superiority against two different agricultural pests; two spotted spider mites and Beet army worm compared to commercially available formulations. The efficacy was remarkable after longer period of time demonstrating their sustained mode of drug release from worm micelles.

COLL 327

Supramolecular photovoltaic cells: Synthesis, self-assembly, and theory-experiment evaluation

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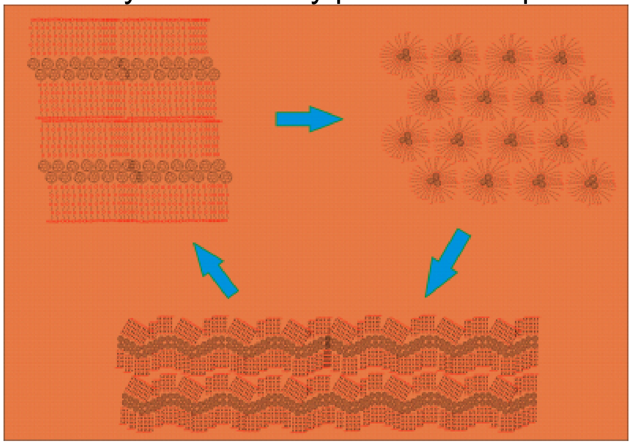
A new family of solar cells in which the components self organize into nanometer scale patterns that generate different supramolecular phases by cycles of

assembly-disassembly processes is presented.



Their theory, synthesis, characterization, physical properties and photo-voltaic efficiency as a function of their supramolecular structure are presented and analyzed. The key features of the design such as self-organization, polymerization, radical transfer and assembly-disassembly properties to achieve a defect-free system will be emphasized.

COLL 328

Functional FePt nanoparticles enable CT/MRI dual modal molecular imaging

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Water-solvable FePt nanoparticles in diameter of 3, 6, and 12 nm (3 nm-, 6 nm- and 12 nm-FePt) were applied as a dual modality contrast agent for CT/MRI molecular imaging. All FePt nanoparticles revealed the excellent biocompatibility in cytotoxicity and hemolysis examinations. The results of bio-distribution showed the highest serum concentration and circulation half-life for 12 nm-FePt. Moreover, the amounts of FePt nanoparticles in major organs were very sparse after 168hr. FePt nanoparticles conjugated with anti-Her2 performed molecular expression through CT/MRI dual contrast effect in the MBT2 cells with high endogenous Her2 expression and its Her2/neu gene knock out counterpart. The results revealed that CT/MRI contrast effect of 12 nm-FePt outperformed that of 3 nm-FePt. The selective contrast enhancement of Her2/neu overexpression cancer lesions in both CT and MRI was found in tumor bearing mice after tail vein injection of 12 nm-FePt conjugated with anti-Her2. With respects to the MR images before injection, a decrease of tumor lesion intensity to 51% was

observed at 24 hr after the injection. On the other hand, a 138% contrast enhancement of the tumor lesion at 24 hr after targeting was observed in CT imaging

COLL 329

Formation of metal ion complexes with plant phytohormones and green synthesis of nanoparticles for cellular detection

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Plant based-biocompatible phytohormones and polyphenols were used for the fabrication of a wide range of metal nanoparticles, such as gold, silver, copper, palladium, and platinum, as well as bimetallic nanoparticles such as Au-Pd and Au-Pt. The growth of the nanoparticles was probed over a period of time using spectroscopic methods and electron microscopy. In some cases the phytohormones were self-assembled prior to mineralization to provide a template for the growth of the nanoparticles. Depending upon the growth conditions nanofibers, nanovesicles or microtubules of phytohormones were formed. The formation of the nanoparticles was also compared in the absence of templates, where different concentrations of the metal ions were incubated directly with the phytohormones. It was found that in some cases, shaped nanoparticles, such as hexagonal nanoparticles, as well as assemblies of nanochains were formed. This method lends itself to direct application for optoelectronics and sensing for cellular detection and drug delivery.

COLL 330

Pseudo-polyelectrolytes: Introduction and application

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The use of weak polyelectrolytes in multilayer polymer systems provides a means of altering the physico-chemical properties of these thin films. We have examined the limits of the polyanions by incorporating the pseudo-polyelectrolytes (pPE), poly(4-vinylphenol) (PVPh), into multilayer systems with either the weak polyelectrolyte (WPE), poly(allylamine hydrochloride) (PAH) and the strong polyelectrolyte (SPE), poly(diallyldimethylammonium chloride) (PDADMAC) from dilute aqueous media. Since PVPh exhibits moderate antimicrobial ability, we tested these newly developed multilayered systems to

determine their ability to act as antimicrobial surface coatings. For the PDADMAC/PVPh multilayered coatings, >70% inhibition of growth of *S. epidermidis* was observed at an assembly pH of 10.5 and 11.0. In addition, we have been able to exploit the lowered pKa of the alcohol of poly(norbornenyl hexafluoroisopropylmethyl alcohol) (HFIPA) and successfully multilayer with both PAH and PDADMAC.

COLL 331

Interfacial polymerization to enhance immunofluorescent staining

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Here, we describe a novel approach towards cell and tissue staining based on interfacial polymer networks. Our approach exhibits exceptional detail of protein localization at antibody concentrations several orders of magnitude lower than typical immunofluorescent protocols. In this novel approach, a polymerization photo-initiator conjugate is coupled to the region of antigen expression through specific biological interactions (protein-protein or protein-small molecule). Next, monomer is added to the sample and the sample is illuminated to cause the initiator to form radicals rapidly. A large amount of labeled polymer is formed specifically in regions expressing the target antigen. We will demonstrate the effectiveness of this approach in the staining of both large regions of cytoplasm and small localized protein structures on the nuclear envelope. We will also discuss characterization of the polymeric labeling system.

COLL 332

Real-time mechanically-induced cellular remodeling

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Cellular adaptations to the local microenvironment induce realignment of the cell cytoskeleton and redistribution of cell adhesions, altering the cellular structure-function relationship. The ability to measure real-time mechanosensitive events at sub-cellular level in response to discrete and physiologically relevant mechanical stimulation is the critical component in understanding mechanically-

induced cellular remodeling. Integration of mechanical stimulation of live cells by an atomic force microscope tip with simultaneous fluorescence imaging enables visualization and quantification of molecular dynamic events at the sub-cellular level. We have shown that mechanically-induced cell signaling across the cell membrane through a matrix-integrin-cytoskeleton linkage alters the intracellular force balance resulting in cytoskeleton and focal adhesion remodeling in live cells. Our results show that different treatments induced distinct modification on focal adhesion and actin fiber distribution. By exploring innovative approaches like these, new information for understanding live cell restructuring and dynamics in response to mechanical force can be provided.

COLL 333

Engineering cell access with nano-functionalized posts

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The cell membrane is one of the most vital components of a cell; the gate-keeper into and out of the cytoplasm. Studies ranging from neural activity to drug discovery to fundamental cell physiology rely upon controlling electronic or chemical flow across this barrier. Unfortunately, our ability to artificially control cellular access is surprisingly poor; current techniques generally involve creating holes in or puncturing cell membranes that often cause rapid cell death. Yet precise, non-destructive access to the cell interior can lead to an impressive range of new techniques and devices, ranging from neural-prosthetic interfaces, electrical cell monitoring for disease, to rapid drug screening. One of the critical problems is that we have little knowledge of the lipid interface with penetrating materials. Here we explore how inorganic materials with nanoscale molecular functionalization interact with and control this vital interface. By selectively tuning the hydrophobicity and flexibility of the molecular functionalization we can replicate many of the design features of natural transmembrane proteins, providing non-disruptive mechanical, electrical and chemical access into the cell. These “Stealth” probes spontaneously insert into lipid membrane, and form tight lipid-post junctions. We will discuss the molecular design, simulation, and testing of different material-lipid interfaces. Force testing with atomic force microscopy (AFM) turns out to provide a quantitative measure the interfacial adhesion, which surprisingly reveals significant adhesion energy differences between molecular groups with similar hydrophobicity but different mobility. This expands metrics necessary for good membrane interfaces beyond the traditional 'hydrophobicity indices'. We also show how these Stealth probes can be fabricated either in large arrays, or as single structures, such as at the end of an AFM cantilever, together with some preliminary results towards new applications of the technology.

COLL 334

AFM study of biomembrane mechanics of epithelial cells

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We will present atomic force microscopy study of mechanics of human epithelial cells collected from skin and cervix. The AFM method will be described to investigate mechanical properties of aging skin cells. We demonstrated that the use of a relatively dull colloidal AFM probe is essential to attain the correct value of rigidity. We will demonstrate that the found previously increased rigidity of old skin cells is well correlated with higher density of cytoskeletal fibers in the cortical layer of the membrane, and almost uncorrelated with the total volume of cytoskeleton. For the case of cervical cells, cell membrane is a more complicated and has to be treated as a brush layer. We will describe the appropriate method to extract information about this membrane layer from the AFM data.

COLL 335

Deformable surface micropatterning for cell force measurement and tumoral transformation investigation

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Cell ability to exert traction forces on their microenvironment through the development of intra-cellular tension strongly impacts cell physiology and notably tumoral transformation. Current methods to measure cell traction forces rely on the deformation of soft substrates. Exact forces can not be directly inferred from deformation since local deformation result from both local and distant force application sites. Accurate measurements require either long calculations or sophisticated microfabrication steps to numerically or physically separate force application sites. We developed a new method to associate the control of the spatial distribution of cell traction forces on adhesive micropatterns with force measurement on soft deformable substrates. Cells pull on the micropattern and, on appropriate geometries, contract micropattern length in a standardized fashion. After a calibration of the force-deformation relationship, cell traction forces could be rapidly and accurately quantified by a single micropattern picture acquisition and length measurement. We applied this method to the

measurement of traction forces in hundreds of epithelial cells in various conditions mimicking specific tumoral transformations. We found that, contrary to the current view, all transformation phenotypes were not associated to increased level of cell contractility.

COLL 336

Nanomechanical properties of supported lipid bilayers

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Quantification of the mechanical stability of lipid bilayers is important in establishing the composition-structure-property relations, and shed light on understanding functions of biological membranes. A direct correlation of the self-organized structures has been demonstrated in phase-segregated supported lipid bilayers consisting of dioleoylphosphatidylcholine/egg sphingomyelin/cholesterol (DEC) in the absence and presence of ceramide (DEC-Ceramide) with their nanomechanical properties using AFM imaging and force mapping. Owing to its capability for simultaneous determination of the topology and interaction forces, AFM-based force mapping was used in our study to directly correlate the structures and mechanical responses of different coexisting phases. We have designed an experiment to directly probe and quantify the nanomechanical stability and rigidity of the ceramide-enriched platforms that play a distinctive role in a variety of cellular processes. Our force mapping results have demonstrated that the ceramide-enriched domains require both methyl β-cyclodextrin (MbCD) and chloroform treatments to weaken their highly ordered organization, suggesting a lipid packing different from typical gel states. We further explored the influence of different cholesterol levels (5-40%) on the morphology and nanomechanical stability of phase-segregated DOPC/SM/Chol bilayers. We obtain breakthrough forces of the coexisting phases: SM/Chol-enriched liquid ordered domains (Lo) and DOPC-enriched fluid disordered phase (Ld), at various loading rates. The breakthrough activation energies (ΔU) were calculated following the model for rupture of molecular thin films, and compared favourably with the reported values for the elementary processes involved in biomembrane and model membrane fusion using different techniques. References: 1. Sullan, R.M.A.; Li, J.K.; Zou, S. *Langmuir* 2009, *25*, 7471-7477. 2. Sullan, R.M.A.; Li, J.K.; Zou, S. *Langmuir* 2009, *25*, 12874-12877. 3. Ira; Zou, S.; Carter, D.; Vanderlip, S.; Johnston, L. *J. Struct. Biol.* 2009, *168*, 78-89. 4. Sullan, R.M.A.; Li, J.K.; Hao, C. C.; Walker, G. C.; Zou, S. *Biophys. J.* 2010, *99*, 507-516.

COLL 337

Regulation cellular signaling via engineered nanostructures of protein

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Understanding the impact of engineered extracellular matrix structure and geometry on the propagation of the signal process is important in guiding cellular behaviors. Here, focal adhesion mediated cellular signaling of NIH 3T3 cells was regulated via engineered assemblies of fibronectin (FN). As an example, FN line pattern with a width of 850 nm and separated by 650 nm was fabricated using microcontact printing followed by selective protein immobilization. Two distinguished differences were observed when comparing patterned surface to conventional FN surface prepared by soaking. Individual cells significantly elongated along FN lines, indicating that cell spreading and local movement follows the FN pattern. Bundles of actin filaments follow the direction of the FN lines, which suggested cytoskeleton re-organization due to mature focal adhesions is guided by the FN ligand underneath. This presentation will also discuss effects of various sizes and geometries of FN micro/nanostructure on the downstream cellular signaling pathways.

COLL 338

Cells in motion: Live cell interferometry (LCI)

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Over the past several years, we have begun to use interference microscopy to augment atomic force microscopy as a tool to the study the mechanics and dynamics of single live cells and groups of cells. This technology is extremely well suited to capture motion on the micro- and even nano-scale, under certain conditions, with a temporal dynamic range and field of view that far exceeds scanning probe techniques. We will present results showing the application of LCI to measurement of whole cell mechanical properties, label-free tracking of cytosol flows within cells and sub-pico gram-sensitivity, dynamic cell mass measurements.

COLL 339

Cellular nanomechanics as drug sensitivity marker for ovarian cancer

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Ovarian cancer is the most lethal of gynecological malignancy and a chemotherapy-sensitive disease with about 85% patients responding to first line treatment, consisting of a combination of platinum agents. Primary platinum resistance in 15% patients and development of platinum-resistance in recurrent ovarian cancer presents a major therapeutic challenge. A major obstacle facing ovarian cancer management is the lack of predictive markers to determine the sensitivity of ovarian cancer cells to a specific chemotherapeutic regimen. Cell stiffness, is a newly recognized cellular phenotypic event associated with cytoskeletal organization. AFM has been used previously to study cellular events on cell lines as well as cancer cells obtained from actual patient samples*. Using in vitro drug-sensitivity model systems we show that platinum based treatment of ovarian cancer cells increases the cell stiffness. The findings suggest potential of nanomechanical profile as marker of cancer drug sensitivity. **Cross, S.E., Gimzewski, J.K. Nat Nano 2, (2007)*

COLL 340

How excellent mentoring by PhD advisor Bob Good inspired my carieer

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In 1970 I received my PhD degree under the superb mentorship of Dr. Robert Good. The dissertation included the development of a thermodynamic model predicting surface free energy produced by different surface roughness conditions. This research also lead to the discovery of the "smear layer" on cut tooth surfaces, which has a major influence on the wetting and adhesive properties of dental adhesives. My research has continued in this area and has lead to the develoment of a new low stress silorane dental composite . This material has superior biocompatiblity and low polymerization stress properites comparied to PMMA and has progressed to the development of a new bone cements for orthopedic applications. Federal funding for this research over the past 40 years exceeds $35M and mentoring over 100 graduate students and

junior faculty. Bob Good played a significant role in providing a foundation for me to continue in a successful research career.

COLL 341

Long range interactions and electrodynamics of nanoscale assembly: Carbon nanotubes

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The optical properties and electronic structure of materials are critical as the origin of the electrodynamic van der Waals – London dispersion (vdW-Ld) interactions, the universal long range interaction, which plays a critical role in wetting, interfacial energies, and nanoscale assembly. At the nanoscale, beyond the formation of individual chemical bonds during chemical synthesis, long-range interactions (LRIs), such as the vdW-Ld, electrostatic and polar interactions, dominate the nanoscale manipulation and assembly of materials for functional nanodevices such as made from single-walled carbon nanotubes (SWCNTs). SWCNTs are optically and morphologically anisotropic; we determined the *ab initio* full spectral, uniaxial, optical properties from band structure calculations, then developed anisotropic cylinder extensions of Lifshitz's vdW-Ld formulation to determine the vdW-Ld interaction of 64 SWCNTs. These results show a clear dependence on CNT type (metal or semiconductor), structure (armchair, zig-zag, or chiral), and [n,m] chirality, and new effects such as vdW-Ld torques for CNT alignment.

COLL 342

Surface light scattering spectroscopy of fluid - liquid interfaces

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Robert Good was the editor of an early review (1974) of our work on surface light scattering spectroscopy (SLSS). We now remember Robert through a review of the studies using SLSS that the Case group developed over the last few years. Characterization of phase-grating systems will be discussed in the context of high precision measurements and the integration of SLSS into a Brewster Angle Microscopy system both mounted on a Langmuir trough. We will present the application of SLSS to the CO_2 – water system at elevated pressures and the determination of the Hansen interfacial excess thickness parameter, τ, and its relevance to the engineering of enhanced oil recovery.

COLL 343

Intermolecular interactions, contact angles, and solid surface tensions

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Contact angles are used as an indirect means to determine surface tension of polymeric films. Contact angles of several liquids measured on a solid surface follow a smooth curve when plotted as a function of liquid surface tension ($\gamma_{lv}\cos\theta$ vs. γ_{lv}). Changing the solid, i.e. γ_{lv}, results in parallel curves, suggesting that $\gamma_{lv}\cos\theta$ is a function of γ_{lv} and γ_{sv} only. Thus, an equation of state was developed to determine solid surface tensions in conjunction with the Young equation. Close scrutiny of the smooth curves revealed small deviations of several degrees in contact angles. After establishing that deviations are not experimental errors, we identified molecular interactions at the solid-vapor and solid-liquid interfaces that account for contact angle deviations. Such specific interactions cause the solid-liquid interfacial tension, γ_{sl}, not to be a precise function of γ_{lv} and γ_{sv}. Criteria are proposed to identify test liquids that eliminate specific molecular interactions.

COLL 344

Super-hydrophilic surfaces and materials

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The term *super-hydrophilicity* was introduced soon after the explosion of research on *super-hydrophobic* surfaces, in response to demand for surfaces with exceptionally strong interactions to water. The definition of super-hydrophilic substrates has not been clarified yet, and unrestricted use of this term has stirred controversy in the last few years. In this presentation, we will review the physics behind super-hydrophilic effects and make recommendation on defining super-hydrophilic substrates and surfaces. We will also review chemical and physical methods used in fabrication of substrates on surfaces of which water spreads completely. Several applications of super-hydrophilic surfaces, including examples from the authors' own research, will be presented.

COLL 345

Calculation of contact angle hysteresis on chemically heterogeneous surfaces

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Contact angle hysteresis acts as a static friction for liquid drop motion on solid surfaces. It is a limiting factor in applications such as electrowetting and superhydrophobicity. Causes of hysteresis include chemical heterogeneity and roughness of the solid, and sorption. There is no general theory to predict the hysteresis exhibited by a surface of known properties. For chemically heterogeneous surfaces, calculations have been made for certain special cases, such as alternating stripes, checkerboard patterns, or dilute distributions of defects. We present a new computational approach that calculates advancing and receding contact lines on a specified solid surface by moving the contact line down the steepest gradient in free energy. The method allows hysteresis to be calculated for surfaces of arbitrary heterogeneity, as long as the contact line deviates by relatively small amounts from its average position. It enables exploration of general relationships between surface energetics and hysteresis.

COLL 346

Effects of microdroplet interfacial properties on the performance of digital microfluidic biochips

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Digital microfluidic biochips are a new generation of miniaturized biomedical platforms. These devices are based on the transport of discrete microdroplets using the electrocapillary force. One of the biggest challenges for these biochips is preventing nonspecific adsorption of biomolecules onto electrode surfaces through hydrophobic and electrostatic interactions. Adsorption arising from both interactions can influence the contact angle which will ultimately decrease the device performance. Therefore, real-time characterization of the microdroplet interfacial properties is a crucial task in the successful design and control of these devices. In this paper, a new methodology for characterization of microdroplet interfacial properties in digital microfluidic systems is proposed. The proposed methodology relies on the contact angle measurement using an enhanced Automated Polynomial Fitting (APF) method, and relates the microdroplet interfacial properties to the microdroplet electrohydrodynamics. The

results show that the device efficiency drastically increases due to the implementation of the interfacial property measurement submodule.

COLL 347

Interfacial phenomena in photolithographic processes: Characterization by contact angle and streaming potential measurements

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The continued shrinking of dimensions in the photolithographic process is a challenge in microelectronic fabrication. Current hot topics such as the collapse of photoresist patterns and blob defects are closely related to the surface properties of chemically amplified resists (CAR) and bottom anti-reflective coatings (BARC) as well as to the interaction of these surfaces with developer and rinse liquids. By adding anionic surfactants directly into the developer solution or using a cationic surfactant rinse, both types of defects could be considerably reduced. It will be shown that the combination of contact angle with streaming potential measurements is a powerful strategy to study the interfacial phenomena at solid/ liquid interfaces in these systems. In this way, changes in the hydrophilicity/ hydrophobicity measured by advancing and receding contact angles and in the surface charge (acid-base properties) could be quantified and were successfully used to explain the effect of surfactants.

COLL 348

Phase rule for systems containing surface and line boundaries

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Using devices to perform small-volume chemistry was first proposed by analytical chemists, who coined the term “miniaturized total chemical analysis systems” (µTAS) for this concept. Recent research efforts have included the possibility of imparting higher levels of functionality by making features in different materials and at different levels within a device to integrate electrical or electrochemical function into chips for purposes as diverse as heating, temperature sensing, electro-chemical detection, and pumping. In thermodynamics, the phase rule curtails the number of independent, intensive variables that determine the state of these devices. Such relations are useful conceptual tools for the classification and derivation of a host of relations between temperature, pressure and composition for co-existing, multi-component phases. Two well known examples

are the Clausius-Clapeyron equation and the Duhem-Margules equation. This paper generalizes the classical Gibbs phase rule to small systems with multi-phase boundaries and considers the implications for both the measurement of line tension and µTAS.

COLL 349

How does lung surfactant reach very low surface tensions? New evidence from comparative AFM study

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Lung surfactant is a complex phospholipid-protein mixture that coats a thin film at the air-water interface of the lung. The main function of the surfactant film is to reduce alveolar surface tension to very low near-zero values, thus stabilizing alveoli against collapse. In spite of the consensus on the very low surface tension in the lung, the biophysical and physicochemical mechanisms by which lung surfactant films, containing only less than 50% disaturated phospholipids, reach such low surface tension are still unknown. We studied the biophysicochemical mechanism of lung surfactant films using atomic force microscopy. By comparing surfactant preparations with various biochemical compositions, including pure dipalmitoyl phosphatidylcholine, a synthetic model surfactant, animal-derived clinical surfactants, and endogenous bovine natural surfactant, we concluded that lung surfactant reaches low surface tension by squeezing out fluid phospholipids and forming multilayers closely attached to the interfacial monolayer. This process is regulated by surfactant proteins and cholesterol.

COLL 350

Initial bacterial attachment in slow flowing systems: The effects of substrate surface hydrophobicity

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Bacterial biofilm has detrimental effects on human health and industrial productivity. Understanding the initial bacterial attachment is critical in developing strategies for preventing biofilm formation. In this study, we followed the initial attachment of three bacterial species; *Pseudomonas aeruginosa* PAO1, *Escherichia coli* and *Pseudomonas putida*, on two different surfaces, glass and an organosilane modified hydrophobic surface, using slow flowing systems. The hydrophobicity of the bacterial strains was evaluated by both partitioning to hexadecane and contact angle measurements. On the hydrophilic glass surface, the attachment trend was found to be PAO1 < *P. putida* < *E. coli*, while the opposite trend was observed on the hydrophobic surface. The attachment of these three bacterial strains on the glass surface was able to be interpreted by the extended DLVO theory. However, we would need to consider the energy barrier, from the secondary minimum to the primary minimum, to explain the initial attachment trend on the hydrophobic surface.

COLL 351

Contact angle phenomenon at sharp edges: A thermodynamic approach

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An edge is known to hinder a sessile drop's spreading, which means apparent contact angle can exceed the advancing contact angle value. Understanding of the edge effect is important for designing superoleophobic surfaces A free energy model has been developed to investigate energetic state of drops on a single pillar (cylindrical, upright frustum, and inverted frustum geometries). An analysis of drop free energy levels before and after crossing the edge, allows us to understand the contact line pinning and depinning phenomenon. From this, we learn how the contact angle will change at the sharp edges. In particular, it is found that with changing the edge angle, i.e., the angle subtended by the two surfaces forming the solid edge, three possible drop spreading behaviors at the edge are possible.

COLL 352

Science and engineering: The contributions of Dennis Prieve to colloidal systems

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@font-face { font-family: "Calibri"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 10pt; line-height: 115%; font-size: 11pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } The slogan “small is good” has guided Dennis Prieve's research into the fundamental issues at the colloidal level that control macroscopic phenomena. He has made seminal advances in our understanding of how colloidal particles interact with each other and the surfaces

that bind them. While Prieve's name is linked to the development of total internal reflection microscopy (TIRM) and its application to the study of colloidal equilibrium and dynamics, the range of his contributions is broader. In this presentation I draw on my ground-level observations to comment on several major advances from his work, from electroless deposition of paint to directly measuring the statistical motion of particles near boundaries.

COLL 353

Measurement of critical Casimir forces with TIRM

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Similar to electromagnetic vacuum fluctuations which can induce long-ranged interactions between uncharged, conducting surfaces, its classical analogue was predicted almost 30 years ago to occur in confined binary mixtures close to their critical point. This so-called critical Casimir effect has attracted considerable attention because it can strongly modify the interaction potential of colloidal particles immersed in a binary fluid. We present the first direct measurement of such forces between a colloidal particle and a flat surface in a water – 2,6-lutidine mixture obtained by a TIRM experiment. Upon approaching the critical point we observe long-ranged interactions which are attractive or repulsive depending on the specific boundary conditions of the walls which can be continuously varied by small modifications of the confining surfaces. When small amounts of salt ions are added to the critical mixture we find strong changes in the measured interactions. This suggests a strong coupling between the ion concentration and the critical fluctuations which may open novel possibilities for tuning interactions in charge-stabilized systems.

COLL 354

Loops, tails and trains: A simple model for structural transformations of grafted adsorbing neutral polymer brushes

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The structure of grafted adsorbing polymers on surfaces is described as a statistical ensemble of loops generated by a one dimensional random walk perpendicular to the surface. The configuration of each chain is considered as a succession of closed loops ended by an open loop (a tail). The probability of

formation of each individual loop is the product between the probability of first return to the surface and a Boltzmann factor containing the free energy of the Flory-Huggins kind, which is approximated by the minimum free energy of all possible configurations of that loop. At high grafting densities, the attractive interactions between monomers and surface control the fraction of polymer belonging to either closed loops or tails, hence the formation of a stretched grafted brush. At low grafting densities, the increase of that interaction above a critical value generates an abrupt collapse of the brush on the surface. Whereas for long polymers (with more than about 100 Kuhn segments), the structure of the brush can be determined, in general, only via Monte-Carlo sampling, it is argued that the two structural transitions indicated above can be well predicted by simple approximations.

COLL 355

How surface forces control the coalescence of bubbles

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Bubbles represent one of the simplest and most pervasive entities in the world around us. Despite their prevalence in nature and in numerous industrial processes, the behaviour of bubbles is still incompletely understood. This is mainly due to the difficulty in developing sufficiently accurate and reproducible experimental techniques for their examination. Here we report direct observations of controlled collisions between two micro-bubbles in water to elucidate the effect of gas type and solution pH on their stability against coalescence, using pure CO_2, air, nitrogen and argon. Bubble coalescence appears to be strongly linked to the presence of CO_2: whereas inert gases behave as predicted by charge repulsion from adsorbed ions, pure CO_2 bubbles are considerably more stable than predicted. Significantly, the trace concentration of CO_2 in air strongly biases its behaviour away from that of the inert gases. The stability of CO_2 bubbles cannot be explained by charge alone, suggesting an additional mechanism.

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Manufacture of particle stabilised droplets

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Particles are known to act as stabilisers of droplets through adsorption at the interface. In many cases, the adsorption is a desired effect, for example in the production of some emulsified products. On the other hand, without control this can also be an unwanted effect, for example in drop-on-demand inkjet printing. In many of these processes, successful control is needed on well-defined timescales and, as a result, we have been exploring aspects of the kinetics of adsorption for particles at interfaces. Using examples from our recent research, issues associated with particle attachment at both liquid-liquid and liquid-air interfaces will be presented. The implications of these findings for the production of particle stabilised droplets will be discussed.

COLL 357

TIRM mimic for nanoscale interrogation of “soft” interfaces

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In this talk, we will describe how we have used a TIRM mimic, total internal reflection fluorescence microscopy or TIRFM, to investigate a variety of fundamental phenomena at interfaces that could be described as “soft” or “fluid-like,” including protein adsorption at the oil-water interface, optical and electrochemical characterization of biomimetic interfaces, and the dynamics of imbedded fluorophores in various active nanostructures. We will also discuss how we have used parallel experiments in this system and in a time correlated single photon counting (TCSPC) apparatus to provide complimentary data that significantly improve our understanding of labeled moieties in liposomes and in reconstituted bilayer lipid membranes.

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Particle height measurements with alternating electric fields using TIRM, the key to understanding AC electric field induced forces on particles near surfaces

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An alternating electric field applied to a suspension of colloidal particles near a planar electrode can surprisingly induce lateral forces, leading to aggregation or separation of the particles. Although this effect had been measured by several research groups, none of the (conflicting) results could conclusively demonstrate the cause of the lateral motion. When I started as Dennis' and Paul Sides' student, I used total internal reflection microscopy (TIRM) instead, measuring the vertical motion of single particles under the same ac fields. We found that the vertical motion clearly correlated to direction of lateral motion. At frequencies < 1 kHz in particular, a phase angle between the expected motion and the observed motion proved decisive in identifying the primary source of the lateral motion. Finally, using a model we demonstrated that the phase angle in the vertical motion of the particles was the key factor in determining the driven inter-particle motion.

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Colloidal stability at high electrolyte concentrations

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The classic theory of colloidal stability predicts that colloidal suspensions stabilised by electrostatic repulsions have a stability ratio W which is a steep function of surface potential (or surface charge) away from the coagulation region around the isoelectric point. Several well characterized systems experimentally exhibit this steep rise from coagulation to stability at low electrolyte concentration (~10^{-3}M) but a distinctly slower rise at higher concentrations (~10^{-1}M) in contrast to the predictions of conventional DLVO theory. Recently Michal Borkovec has postulated that the discrepancy is due to the fact that the interaction energy maximum which controls the stability ratio W occurs at much closer separations of the interacting particles (~κ^{-1}) at high electrolyte concentration. It is therefore more sensitive to the distribution of charge on the particle surfaces which is assumed uniformly distributed in the classical stability theory. For low electrolyte systems where the energy maximum occurs at greater separations the uniform assumption would seem quite appropriate. We outline a theory of electrostatic repulsion between surfaces which takes into account the patchiness of the surface charge distributions and does not assume the patches sit on regular surface lattice sites. We calculate the stability ratio dependence on average surface charge density as the dimensions of the patches are varied for various electrolyte concentrations and compare this discreteness of charge effect with the classical theory.

COLL 360

Solar energy harvesting with nanoparticle/polymer composite bulk heterojunctions

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We describe the use of both semiconducting and metallic nanoparticles in composite bulk heterojunction solar cells. While CdSe has been widely studied as an electron acceptor in polymer/quantum dot blends, other inorganic nanoparticles, including low band-gap and non-toxic earth abundant semiconductors have exhibited substantially lower performance. We present photoinduced absorption data demonstrating that this is often due to poor charge separation efficiencies at the organic/inorganic interface, and indentify new polymer/quantum dot composites with substantially improved performance characteristics. Finally, we show that plasmon-resonant metal nanoparticles can also be used to effectively increase light harvesting and charge generation in optically thin semiconductor films, and suggest variety new synthetic targets for incorporating semiconductor and metal nanostructures into thin film solar cell structures.

COLL 361

Optically active metallic nanostructures as platforms for efficient coupling of thermal and photonic stimuli for energy efficient chemical conversion

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Recent progress in solution-based synthetic techniques has allowed the synthesis of Ag nano-structures with well-controlled, highly uniform sizes and particle geometries. These Ag particles exhibit a strong localized surface plasmon resonance (LSPR) due to the nanometer scale spatial confinement and the metal's inherent electronic structure. For nanometer-sized Ag structures, the resonance frequency falls in the ultraviolet to visible light range, and it can be tuned by changing the geometry and size of the Ag particles. The excitation and subsequent decay of surface plasmon states is manifested through three resonant processes: (a) non-radiative decay: absorption of photons which excite phonon modes, lattice vibrations, that locally heat the particle, (b) radiative decay: Rayleigh scattering process where photons are concentrated at the surface of the particle and scattered in high intensity in the vicinity of the particle without being degraded into heat, and (c) direct transfer of electrons from plasmon states to surrounding, electron-acceptor medium. In this work we will show examples of how the shape and size of Ag nanostructures can be tuned to allow different decay mechanisms to drive photocatalytic reactions. In the first

case large Ag nanostructures (>75 nm) are utilized to take advantage of the efficient scattering cross sections (mechanism b) to enhance photochemistry on neighboring TiO_2 nanoparticle photocatalysts. In another example we will discuss the utility of mechanism c to drive important industrial oxidation reactions directly on Ag nanoparticles at temperatures below what is necessary in pure thermocatalytic reactions.

COLL 362

WITHDRAWN

COLL 363

Semi-transparent metal nanostructures as alternatives to transparent conducting oxides in organic photovoltaic devices

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Semi-transparent metallic, nanostructured, hole-selective contacts are intrinsically more conductive, more chemically stable, easier to modify, and significantly less costly than their transparent conductive oxide (TCO) counterparts traditionally used in organic photovoltaic (OPV) devices. In this work, gold nanowire, nanogrid and honeycomb nanostructures composed of a high work function materials were developed and explored as hole-selective contacts in OPVs. These structures show optical transparency and sheet resistance comparable to those of traditional TCOs that can be easily tuned by varying structure geometry, such as nanowire spacing or nanohole diameter. Results for power conversion efficiency and incident photon current efficiency (IPCE) will be reported for planar heterojunction OPV devices fabricated using these semi-transparent metallic nanostructures as hole-selective contacts and correlated to performance by conventional TCO based architectures.

COLL 364

Charge transport properties in ZnO-based photoelecttrodes for dye-sensitized solar cells with different heat-treatment

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Neck of sintered nanostructured oxides in a mesoporous oxide film as a photoelectrode for dye-sensitized solar cells is very important in terms of transport and life time of electrons in the conduction band of the oxide. In this study, we investigate variations in charge transport properties such as charge transport resistance and electron life time when hierarchical ZnO rod aggregates experience different sintering behaviors, inducing different necking behaviors among the oxides. As ZnO is a sensitive oxide to annealing, it was observed that the increase in annealing temperature from 200 °C to 450 °C causes shape change from rod to sphere as well as neck growth resulting from densification. SEM, EIS, IMPS and IMVS are used to characterize different sintering behaviors and charge transport properties of the ZnO rod aggregates annealed at different temperatures and we present the relationship between cross-sectioned area of the neck and charge transport properties.

COLL 365

Fabrication of radial core-shell Au-TiO_2 nanowires and application in dye sensitized solar cells

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Vertically aligned Au-TiO_2 core-shell nanowires were synthesized by using a two step mechanism. Au nanowires were first synthesized using galvanostatic constant current electrodeposition. A shell of anatase TiO_2 was subsequently grown on the Au nanowires using pulsed laser deposition (PLD). The core-shell nanostructures were then characterized using FESEM, XRD, HRTEM and SAED techniques. The results show that the ~ 200 nm diameter by 2 μm long wires were highly aligned and well separated. The TiO_2 shell was approximately 20-40 nm thick. Dye sensitized solar cells were then fabricated using the core-shell nanowire arrays as photoanode, N535 dye as the sensitizer, and I_3^-/I^- as the redox couple. The Au nanowires inside the highly crystallineTiO_2 anatase nanoshell provided a direct conduction path and improved transport for electrons between the thin TiO_2 shell and the conducting substrate. This efficient electron conduction out of the oxide semiconductor enhanced the current generation as well as the power conversion efficiency of the cell.

COLL 366

Cation-doped titania thin films for solar energy applications

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The objective of this research is to synthesize TiO_2 nano-structured thin films with properties tailored for the photoreduction of CO_2 to CH_4 under UV and visible light. Our efforts are guided by the objectives of (a) creating a high number of photoactive sites, (b) optimizing charge separation, and (c) increasing response to visible light for improved photo-efficiency. Unbalanced reactive dc magnetron sputtering with partial pressure control of oxygen is utilized to fabricate mixed-phase TiO_2 films with novel nanostructures, high solid-solid interfacial areas and enhanced oxidative and reductive activities. Recent studies have focused on cation substation (Nb) in titania to influence photoresponse and photocatalytic performance. We will report on the structural and functional characterization of these films, including: optical response, charge carrier-density, recombination rates, and photocatalyic performance for photo-oxidation and photo-reduction. We will also report on the photoactivity of graphene/Nb:TiO_2 composites.

COLL 367

Aggregation and gelation of polymer colloids under shear

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The science of colloids has indeed made significant advances in recent years and many interesting phenomena are now quantitatively understood. However, conditions involving high solid content and shear are almost systematically avoided in the scientific literature, although these are of specific interest in most industrial applications, probably because of the experimental difficulties inevitably involved in their investigation. On the other hand, under these conditions polymer colloids offer an amazing variety of unexpected phenomena whose interpretation allows uncovering new future in the soft matter behavior. In this seminar various phenomena exhibited by polymer colloids at high solid content and shear are discussed. These include the critical transition in the aggregation behavior of the colloids when moving from Brownian to shear controlled aggregation, or else as the particle size changes from a few to hundreds of nanometers. This transition is investigated both experimentally and through a proper population balance model. This includes both breakage and aggregation kernels, the latter of which includes both Brownian and shear aggregation for particles with DLVO type interactions. The emergence of a rather unique double particle size distribution observed experimentally is confirmed by the model simulations. In the case of sufficiently concentrated colloids, gelation can occur. Critical conditions for gelation and their

dependence on the particle interaction potential in terms of both salt concentration and aggregate mechanical strength are also investigated. Instances where these fundamental concepts are relevant in industrial applications, such as emulsion polymerization reactors and coagulators, are discussed.

COLL 368

Crystallization of semi-crystalline polymers inside colloidal microspheres of polymer nanocomposite

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Microspheres of polymer nanocomposites (blends, organic/inorganic) are widely used as encapsulation and delivery vehicles in applications such as coatings, cosmetics, drug delivery, liquid and dry toners. Structural organization (e.g. crystallization) of constituents within such microspheres is often critical to their performance in end uses. Here we report on crystallization behavior of semi-crystalline polyesters confined within colloidal microspheres produced through a novel colloidal aggregation/annealing process in water. In this approach, crystallization temperature, annealing time, and annealing medium (water, organic solvents, ionic liquids, etc) can be easily changed to produce “designer” polymer crystal morphologies with well-controlled crystalline domains and spatial distributions.

COLL 369

Model bead-spring colloidal chains

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We have recently developed a system consisting of chains of patterned magnetic colloids linked together with DNA. This system provides a model bead-spring-bead model to study polymer dynamics. These chains can be tuned so that they exhibit varying rigidity and are capable of folding with specific chemical and biorecognition signals. The formation mechanism and stability of these DNA-linked paramagnetic particle chains will be described. A model for the total energy landscape to describe the inter-particle interaction potentials that include DLVO potentials, steric repulsions between surface DNA, and potential of DNA

bridging between particles describe the chain behavior over a wide range of magnetic field strengths and surface DNA lengths. Also we will describe the use of the lactose repressor protein (LacI), a DNA binding protein, which functions as a negative transcription regulator, to modulate the flexibility of the colloidal chains. Comparison between expected and observed diffusivity behavior will be given.

COLL 370

Dynamics of phase separation in oat beta–glucan⁄milk mixtures studied with ultrasonics and diffusing wave spectroscopy

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Macroscopic phase separation due to thermodynamic incompatibility occurs when beta–glucan (BG) is mixed with milk proteins. The evolution and coarsening of phase separating domains were investigated in milk using ultrasonic and diffusing wave spectroscopy, allowing the observation of the dynamics of phase separation, *in situ*, without dilution. There is an initial decrease in turbidity parameter (1/l*) and diffusion coefficient of samples by increase in BG concentration. 1/l* increased in samples which showed phase separation up to 0.3% BG, while it was stable at higher concentrations, revealing retardation of the dynamics due to high viscosity developed in the continuous phase. The ultrasonic attenuation and velocity of milk particles revealed the changes in the domains at longer length scales, confirming stability at high concentrations of BG. It is evident that these techniques allow for fine–tuning of structural changes in colloidal mixtures.

COLL 371

Stability of oxidized single-walled carbon nanotubes in the presence of simple electrolytes and humic acid

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The stability of nanoparticles is closely related to the fate, transport, and bio-toxicity of nanomaterials in the aquatic environment. The aggregation kinetics of oxidized single-walled carbon nanotubes (O-SWCNT) was investigated in the presence of humic acid (HA). Results indicated that O-SWCNT was relatively stable in water with critical flocculation concentration (CFC) of 0.16, 4.2×10^{-3} and 5.4×10^{-5} M for NaCl, $CaCl_2$ and $AlCl_3$, respectively. The presence of HA enhanced the stability of O-SWCNT dependent on the type of electrolyte present. The CFC of NaCl increased from 0.16 in the absence of HA to 0.19, 0.23, and 0.25 M when the concentration of HA was 1, 5, and 20 ppm, respectively. However, the effect of HA on the aggregation of O-SWCNT was negligible in the presence of $CaCl_2$ and $AlCl_3$. The findings highlighted the importance of surface treatments, water chemistry, and the presence of NOM on the aggregation behavior of nanomaterials.

COLL 372

Unsaturations of lipids as natural thermal sensors: Adaptive response behavior of a biobased amphiphile

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Life is a process driven by response to touch, temperature, light etc. Natural systems utilize their characteristic unsaturations in the lipids, as a tool to execute such elegant process. Deciphering the stimuli responsive character of biological systems not only shed light on the underlying mechanism in the race for survival of the fittest, but also provides clues to generate unique functional materials in the laboratory. Herein we report fusogenic vesicles from a biobased surfactant N-cardanyl tauramide (NCT), obtained by the judicious combination of cardanol (a renewable phenolic lipid) and taurine (a vital amino sulfonic acid). A reversible, micelle-vesicle transition in response to temperature, followed by vesicular adhesion leading to a sticky jelly phase was observed. An adaptive response behavior of unsaturated alkyl chains present in the cardanol-based amphiphile, much akin to the homeostasis of naturally found lipid membranes has been proposed and corroborated from cryo-TEM and other physicochemical techniques.

COLL 373

Wetting and spreading of nanofluids on solids

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The wetting and spreading of nanofluids comprised of liquid suspensions of nanoparticles have significant technological applications in both nanotechnology and biological systems. This presentation will highlight the complex interactions between the particles in the nanofluid and with the solid substrate. The structural disjoining pressure arises due to the nanoparticle ordering in the nanofluid film confined in the three-phase contact region of a wedge film formed between an oil drop and a solid surface. We use statics analysis which takes into account the contribution of the structural disjoining pressure to analyze the effects of the nanoparticle concentration, nanoparticle size, contact angle, and drop size (i.e., capillary and hydrostatic pressures) on the wetting and spreading behavior of nanofluids. Experiments were performed on the wetting and spreading of nanofluids using advanced optical techniques to validate the theoretical analysis.

COLL 374

Evaporation of the human tear film

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Excess evaporation rates of human tear can lead to dry-eye syndrome. Human tear is covered by a thin oily layer that is thought to reduce evaporate rates. Recent studies claim that films of oily substances play no measureable role in controlling water evaporation. Using a miniature Langmuir trough, we study evaporation rates through thin oil films Evaporation rates are measured gravimetrically at 35 °C for films of thickness ranging from 100 nm (thickness of human meibum) to 100 µm. We confirm reduced evaporation rates. To explain the discrepancy with current literature, we investigate the kinetics of lipid spreading at the water/air interface. Oil initially spreads followed by classical dewetting. On-eye visualization of the human lipid layer also shows dewetting for subjects suffering dry-eye symptoms. We conclude that human lipid reduces tear evaporation rates, but only when uniformly spread. Dewetted oil films do not reduce evaporation rates.

COLL 375

ZetaSpin: Measurement of zeta potential with a rotating disk

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The ZetaSpin is a tool for measurement of the zeta potential of planar disk-shaped samples. Rotating the disk produces streaming current along the plane of the disk and a streaming potential in the vicinity of the disk. Appropriate positioning of sensors allows measurement of the streaming potential and conversion of the measured potential to zeta potential. Invented in 2004, it has found uses and users at Carnegie Mellon and elsewhere both in research and education. The origin and principle of the ZetaSpin are reviewed. Its use for measurement of transient zeta potential and for characterization of consumables for chemical mechanical planarization are described. Streaming potential is a sensitive measure of the adsorption of nanoparticles; the ZetaSpin provides the opportunity to "observe" adsorption of nanoparticles in real time in a geometry having the attribute of uniform accessibility. Theory from the literature is used to correlate the zeta potential with surface coverage.

COLL 376

Optical-tweezers micromechanics: A tool for measuring flow-induced bending of nanotubes

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We measured the elastic modulus of SMA/PEI polymer multilayered nanotubes from the extent of bending induced by a transverse hydrodynamic flow past optically trapped nanotube-microsphere assemblies in overhanging and end-supported beam configurations. Theoretical analysis of the deformation furnished an elastic modulus that we compared to values from dry "nanopaper" sheets, and other polymer multilayer systems reported in the literature. Our results suggest that covalent cross-linking between the SMA and PEI yields water-stable laminates having a higher elastic modulus than previously achieved with polyelectrolyte multilayers. Moreover, the mechanical properties of SMA/PEI multilayer nano-composites are well described by macro-scale continuum theory. Thus, the layer-by-layer synthesis yields laminates, with nanometer scaled layer spacings, for which the bulk elastic modulus can be well predicted from knowledge of the bulk rheological properties of pure SMA and PEI, neither of which forms water-stable nanotubes on its own.

COLL 377

Free energy landscapes for colloidal crystal assembly

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We report the development of umbrella sampling and Fokker-Plank based approaches to model energy landscapes and dynamics in colloidal crystals assembly processes. After identifying appropriate order parameters to monitor colloidal crystallization in the presence of depletion attraction and electric fields, we extract energetic and diffusivity landscapes to capture critical dynamic processes in the vicinity of free energy landscape features (i.e. minima, transition states) and vanishing diffusivities (i.e. dynamic arrest). Results are compared from Monte Carlo, Brownian Dynamics, and Stokesian Dynamics simulations and from video microscopy experiments. We demonstrate the use of these landscapes for describing first passage times between different states as a means to control colloidal crystal assembly processes via open- and closed- loop control schemes that produce defect free single colloidal crystals.

COLL 378

Novel interparticle forces in binary colloidal dispersions

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In this talk, I will discuss the range of forces that can arise between micron-sized colloidal particles (microparticles) immersed in a fluid containing nonadsorbing nanoparticles. Although a relatively simple system, I will show that a wide variety of forces between the microparticles are possible, depending on both the exact nature of the pair potential between the microparticle and nanoparticle, and the nanoparticle concentration. For example, if the microparticle-nanoparticle pair potential is purely repulsive, such as from electrostatic forces between like-charged surfaces, attractive depletion forces arise between the microparticles at low nanoparticle concentrations, while more complex oscillatory forces develop as the nanoparticle concentration increases. By comparison, if the microparticle-nanoparticle pair-potential contains attractive features, such as from van der Waals forces, then the microparticle-microparticle interaction energy at contact can actually be positive relative to infinite separation, which is a manifestation of the so-called nanoparticle halo effect.

COLL 379

Award Address (ACS Award in Colloid and Surface Chemistry sponsored by Procter & Gamble Company). Electrolyte-dependent 2-D aggregation of colloidal particles on a planar a/c electrode

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In an effort to understand the mechanism of 2-D aggregation of colloidal particles observed on a/c electrodes, we have used video microscopy to observe *x,y* motion of isolated pairs of polystyrene latex particles and Total Internal Reflection Micro-scopyto monitor the elevation *z* of a single particle very near one of two parallel, horizontal, ideally polarized electrodes. The direction of motion depends on electrolyte choice: isolated pairs of particles aggregate in solutions of $NaHCO_3$ or KCl and move apart in solutions of KOH, NaOH, H_2CO_3 or NH_4OH. TIRM reveals a phase shift between the electric field and the elevation: in solutions of $NaHCO_3$ or KCl the phase angle is greater than 90º and in KOH, NaOH, H_2CO_3 or NH_4OH the phase angle is equal to or smaller than 90º. Since no faradaic reactions occur, the electrolyte dependence arises from the dependence of the electrophoretic force on ion mobilities.

COLL 380

Fate and transport of nano-TiO_2 in aquatic environments

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Fate and transport of nanoparticles in aquatic environments have been investigated in this study utilizing nano-TiO_2, as it is one of the most widely used nanomaterials in industry. The project was developed to identify the fundamental mechanisms involved in the transport of nano-TiO_2 and the contribution of various environmental parameters including solution chemistry (pH, ionic strength, and ion valence), hydrodynamic effects, and the presence of natural organic matter (NOM). Complementary transport studies have been conducted in both macroscopic (packed-bed column) and microscopic (parallel plate flow cell) systems. Additionally, extensive physical-chemical characterization of the nanoparticles was conducted under these various solution conditions. The combination of these transport and characterization tools has demonstrated the critical role that pH, ionic strength and valence, NOM, and aggregation state play in the transport. Results from both transport systems and particle characterization will be presented, as well as the proposed transport and retention mechanisms observed.

COLL 381

Kinetics and reversibility of multiwalled carbon nanotube deposition on silica surfaces

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Because of their novel mechanical and electronic properties, carbon nanotubes (CNTs) are increasingly used in industrial and commercial applications. To better predict the fate and transport of CNTs in natural and engineered aquatic systems, the kinetics and reversibility of the deposition of multi-walled CNTs (MWNTs) on silica surfaces are investigated. Two batches of MWNTs with different degrees of surface oxidation were prepared in order to compare the effects of surface chemistry on deposition kinetics. The distribution of oxygen-containing functional groups on the MWNTs was obtained using X-ray photoelectron spectroscopy. The deposition of MWNTs on silica surfaces was monitored over a broad range of monovalent and divalent electrolyte concentrations using a quartz crystal microbalance. Critical deposition concentrations were derived and used to quantify the propensity of the MWNTs to undergo deposition. The release of deposited MWNTs resulting from either a change in solution chemistry or hydrodynamic condition will also be discussed.

COLL 382

Transport of engineered nanosilver particles in saturated porous media

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Nanosilver (nAg) is the largest and fastest growing category of nanomaterial, with extensive applications in areas ranging from textiles to medical to construction. Given the ubiquity of nAg, and its potential harmful effects on both humans and the environment, it is incumbent upon us to understand its environmental fate and transport. Due to the importance of groundwater as a pathway from contamination sources to human and environmental receptors, we investigated how different types of nAg (pristine and stabilized nAg) are transported in saturated porous media. In our studies, nAg particles were injected into artificial groundwater flowing through laboratory columns (diameter: 2.5 cm) packed with water-saturated quartz sand to obtain breakthrough curves. Groundwater chemistry was varied to study the effect of the presence of different concentrations of cations and anions on nAg transport. It was observed that transport of stabilized and pristine nAg was different. Filtration theory was used to simulate the transport behavior of the different types of nAg in the quartz sand packed columns. Our results indicate that filtration theory may be applicable to describe the fate and behavior of engineered nAg in porous media.

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CFD modeling of nanoparticle transport and retention through porous media

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In aquatic environment fate and transport of nano-particles (NP) depend on various factors; most important the water chemistry. Ceria, as a model NP, was studied under different conditions in packed sand columns. We used mathematical models to validate and simulate the experimental effluent stream profile. Partial differential equations were solved simultaneously using Mathematica®. The experimental data were accurately simulated using a different numerical model that solves conservation of mass and momentum, and the interaction and deposition of nano-particle with bed material. The mathematical model is based on a specific area-to-volume ratio for the porous media. The model predications were performed using computational fluid dynamic (CFD) software, Fluent®. A comparison of first and second order models were performed to ensure better simulation and more accurate predictions. The model accounted for the attachment and detachment kinetics of NP to the bed and the limiting retention capacity, which was estimated using batch experiments.

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Role of humic substances in controlling the aggregation of capped gold nanoparticles in aqueous systems

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It is well established that natural organic matter (NOM) can strongly influence the colloidal stability of engineered nanoparticles (NPs). Yet, much remains unknown about the mechanisms controlling these interactions. This work aims to deepen our understanding of these processes by correlating the aggregation behavior of engineered (NPs) with physical/chemical properties of the NPs (e.g., capping agent molecular weight and functionality) and humic substances present in the

environment using structure-activity type relationships. Using dynamic light scattering, we have characterized the aggregation of gold nanoparticles stabilized with different capping agents in environmentally relevant aqueous solutions containing NOM from different sources. The influence of NOM on the colloidal stability of capped AuNPs is a function of the organic capping agent, ionic strength and character, and the concentration and nature of the NOM. Our continued work is aimed at understanding the mechanisms controlling interactions between NOM and engineered NPs using advanced spectroscopic techniques.

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Impact of porous media grain size on multi-walled carbon nanotube transport

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The increased production and use of engineered nanomaterials in commercial products will inevitably lead to increased levels of these materials in the environment. Multi-walled carbon nanotubes (MWCNTs) are one class of engineered nanoparticles that are of particular interest due to their light weight, significant strength and excellent conductivity. However there is concern related to the human health and ecological consequences after dispersal of nanomaterials to the environmental as some engineered nanomaterials can have detrimental environmental impacts. Unfortunately there is limited information related to their transport in the environment, and of particular interest to this study, in subsurface systems. The impact of porous media grain size on the mobility of MWCNTs is investigated in one-dimensional column experiments in this study. Experiments were conducted at two representative groundwater velocities commonly found in the field (0.42 m/d and 4.2m/d). The porous media used in these experiments ranged from a coarse textured sand to a very fine sand (d_{50} = 476, 175, 80, 50 µm). In addition ionic strength was varied (0.1mM and 10mM) to better understand dominant MWCNT retention mechanisms. Results of these experiments show that the maximum normalized MWCNT effluent concentration (C/C_0) was always greater than 0.6, suggesting that the MWCNTs were mobile even in the very fine sand. In all cases $C/C_0 = 1.0$ in the low ionic strength column experiments. A numerical simulator that incorporated mechanisms typically associated with colloid filtration theory, in addition to a dual deposition model and a site-blocking term, was used to model observed column results. Results suggest that mechanisms in addition to those associated with colloid filtration theory need to be included in the model to simulate observed

behavior. This study suggests that MWCNTs are much more mobile in subsurface systems than currently assumed.

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Oxygen levels control the dissolution of retained silver nanoparticles in water-saturated columns

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The potential health and environmental impacts of silver nanoparticles, which are used extensively as a biocidal agent in commercial products, highlight the need for a more complete understanding of their fate and transport in the environment. In this work, column experiments were conducted to measure the transport, retention and dissolution of silver nanoparticles (stabilized with citrate) in quartz sands under both oxygen-depleted and -saturated conditions. Borosilicate glass columns (10 cm length x 2.5 cm dia.) were packed with either 40-50 or 100-140 mesh Ottawa sand and completely saturated with either oxygen-lean or –rich water. For each experiment, a pulse (ca. 3 pore volumes) of aqueous suspensions containing ca. 5 mg/L of silver nanoparticles with 3 mM NaCl as the background electrolyte was introduced at a flow rate of 1.0 mL/min, which corresponded to a pore-water velocity of ca. 7.6 m/d. When oxygen levels were low (ca. 1 ppm), dissolved silver ions were not detected in effluent during the course of the experiment. While the silver nanoparticle breakthrough curves exhibited significant tailing, retention increased with decreasing sand grain size, and the concentration of retained silver nanoparticles decreased with travel distance. Under oxygen saturated conditions (ca. 9 ppm), significant amounts of silver ions appeared in effluent samples and elution continued for at least 40 pore volumes. These experimental results demonstrate the dependence of silver nanoparticle dissolution on dissolved oxygen concentration, and the potential for retained silver nanoparticles to slowly release in particulate and ionic forms

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Effects of fractal dimension on nanoparticle aggregation and sedimentation

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Because of their high surface energies, many nanoparticles exist as aggregated clusters in aqueous solutions of sufficient salinity. These nanoparticle clusters are subject to cluster-cluster aggregation. In this presentation, we will discuss how the fractal dimension (d_f) of the clusters affects their aggregation and sedimentation. In our experiments, d_f for nanoparticulate magnetite was controlled either by altering the surface coating of the particles or by changing their oxidation state. d_f of the nanoparticle clusters was determined using synchrotron based small angle X-ray scattering (SAXS), the cluster-cluster aggregation rates were determined using dynamic light scattering, and the sedimentation rates were determined using UV-VIS-NIR spectroscopy. The initial d_f of each suspension was found to be a function of the nanomagnetite surface chemistry as well as the oxidation state. Importantly, the d_f of the clusters changes dynamically as the suspensions are oxidized and these changes should be considered when evaluating nanomaterial fate.

COLL 388

Stabilization of vesicular and supported membranes by glycolipid oxime polymers

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The most widely used method to create long-circulating vesicle carriers is membrane incorporation of lipid-anchored polyethylene glycol (PEG), which sterically blocks serum protein binding, thus preventing lipid extraction, opsonization and immunoclearance. Similar protective effects were previously observed with other lipids with large hydrophilic headgroups such as GM1, though the laborious extraction and synthetic procedures required to access GM1 rendered its application in delivery unpractical. To date, all long-circulating vesicle and nanoparticle applications use PEG-lipids for surface protection, with few improvements to the original system. We report herein new, synthetically accessible glycolipid polymers that provide vesicle stability in serum as well as unprecedented anhydrobiotic and cryoprotective properties: supported lipid bilayers (SLBs) retain uniformity and fluidity after air-drying and and rehydration while glycolipid-protected vesicles survive freeze-drying and rehydration without fusion and minimal contents loss. This methodology employs hydrophilic, charge-neutral, sugar-lipid crosslinking at the lipid headgroup to stabilize membranes. We anticipate that glycolipid systems of this type will be useful for the stabilization of synthetic membranes for delivery and SLB bioanalytical devices.

COLL 389

Regulating membrane function by altering lipid bilayer elastic properties

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Membrane protein function is regulated by the host lipid bilayer. This regulation can be: specific (lipid-dependent), due to specific lipid-protein interactions; non-specific (bilayer-dependent), due to changes in bilayer material properties (bilayer thickness, lipid intrinsic curvature and bilayer elastic moduli); or combination of the two. The bilayer-dependent regulation arises from hydrophobic coupling between a bilayer-spanning protein and the lipid bilayer, which causes protein conformational changes that involve the bilayer-spanning domain to alter the local lipid packing in the vicinity of the protein. The associated bilayer deformation energy contributes to the energetics of the protein conformational change. Because the bilayer deformation energy varies with changes in the chemical composition of the bilayer—including the adsorption of small amphiphiles at the bilayer/solution interface—the bilayer becomes a regulator of membrane protein function. One can measure the energetic consequences of changes in bilayer material properties, as sensed by bilayer-spanning channels, because the bilayer responds to a protein-induced deformation by imposing a restoring force, which can be measured using a suitable reporter. The bilayer-spanning gramicidin channels turn out to be near-ideal reporters because they form by trans-bilayer dimerization, such that the bilayer responds to the deformation associated with channel formation by imposing a disjoining force (F_{dis}) on the channels. Changes in the bilayer deformation energy, and thus F_{dis}, result in changes in the rate constants for channel formation and dissociation, which are measurable as changes in channel appearance rate (f) and lifetime (t). Operationally, changes in bilayer properties that at a constant thickness alter F_{dis} are defined as changes in *bilayer stiffness*. Maneuvers that decrease bilayer stiffness decreases F_{dis}, which increases f and t, and *vice versa* for maneuvers that increase bilayer stiffness. One thus can quantify the amphiphile-induced changes in bilayer material properties in terms of changes in bilayer stiffness

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Nanoparticle disruption of biological membranes

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Nanoparticle interactions with biological membranes are important to understand from the perspective of drug and gene delivery and toxicity. We have employed a

combination of atomic force microsopy, isothermal titration calorimetry, differential scanning calorimetry, NMR spectroscopy, and molecular dynamics simulation to examine the effect of polymer and inorganic nanoparticles on model lipid membranes. We have also employed whole-cell patch clamp to examine the disruption and repair mechanism on the plasma membrane of cells in culture. These physical processes, and their relevance to the area of non-viral gene delivery which relies on nanoscale polymer/DNA “polyplexes”, will be discussed.

COLL 391

Artificial lipid bilayer platforms for human ion channel screening

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We are working to develop artificial lipid bilayer platforms which allow the measurement of physiologically relevant ion channels quickly, easily, and inexpensively. In our initial work, we demonstrated the automated fabrication and measurement of lipid bilayer arrays and the reconstitution and measurement of bacterial pores into them. Our current work centers on measurement of human potassium channels into bilayers. I will discuss our progress in isolating and reconstituting functional potassium channels in bilayers and the prospects of adapting these processes into an automated process flow for ion channel pharmaceutical screening.

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Controlling translocation through nanopores with bio-inspired, fluid walls

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Synthetic nanopores are emerging as promising tools for fundamental and applied studies of individual biomolecules in high throughput; their performance as sensors can, however, currently not match that of sensory nanopores in biology such as ion channel proteins. This talk introduces the concept of synthetic nanopores with fluid lipid walls in an attempt to shorten this gap. The inspiration for this design stems from lipid-coated nanopores in olfactory sensilla of insect antennae. We demonstrate that multifunctional coatings of fluid lipids confer unprecedented functionality to nanopore-based sensors and address currently unmet challenges of single protein investigations with nanopores. For instance, bilayer coatings made it possible to fine-tune and actuate pore diameters with sub-nanometer precision. Incorporation of lipid-anchored ligands

conferred specificity and slowed down translocation of targeted proteins sufficiently to resolve complete translocation events of individual proteins. The biocompatible, fluid nature of bilayer coatings prevented pore clogging and enabled the first translocation analysis of amyloid-beta oligomers. Bilayer coatings also eliminated non-specific binding and facilitated the combined, quantitative analysis of translocation time, volume, charge, and ligand affinity of single proteins.

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Model biological membranes composed of polymerized and fluid lipid bilayers

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Development of a methodology to immobilize biological membranes on the solid substrate is important for a wide range of biomedical applications, such as safety inspection of the food and drugs. We previously developed substrate supported model cellular membranes composed of polymeric and fluid phospholipid bilayers by using a lithographic polymerization of diacetylene phospholipid. Herein we describe the development of techniques to add membrane functions to the model system by chemical modification of polymeric bilayers and incorporation of biological membranes. Polymeric bilayers having ethanolamine groups at their hydrophilic surface could be functionalized with hydrophilic polymers and peptides, giving possibilities to vertically extend the model system. Furthermore, biological membranes could be integrated into the patterned model membrane by using a purposeful mixture of the membrane and detergents. These techniques enable the integration of membrane proteins and should provide possibilities to present membrane functions on the surface in a controlled manner.

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Membrane organization and dynamics in physisorbed polymer-tethered phospholipid bilayers

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Polymer-tethered phospholipid bilayers, where tethering is achieved by physisorbed amphiphilic lipopolymers, represent attractive mimetics of cellular membranes due to their complex dynamic and organizational properties. At low tethering concentrations, the lipid bilayer is uplifted from the underlying solid substrate without notably disturbing its planar geometry. Experiments on integrins are discussed, which illustrate the suitability of such a membrane geometry for the functional characterization of reconstituted membrane proteins with high sensitivity. At high tethering concentrations, physisorbed polymer-tethered phospholipid bilayers show markedly different membrane organization and dynamics, such as pronounced obstruction of protein/lipid diffusion and formation of stable bilayer buckling patterns. Interestingly, in the presence of lipopolymers with moderately hydrophilic polymer moieties, no stable bilayer can be formed at buckling regions, thus causing the compartmentalization of the bilayer into µm-size membrane compartments. Finally, we demonstrate that cholesterol may profoundly impact both obstructed diffusion and membrane organization in these model membrane systems.

COLL 395

Experimental approaches to study the properties of energy storage materials in nanoconfined environments: Modification of ammonia borane in porous silica

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We have investigated Ammonia borane (AB, NH_3BH_3) for its promising hydrogen storage potential (19.6 wt% H_2) and compared its properties in the bulk form to those when infiltrated into the nanopores (4-10 nm diameter) of MCM-41 or SBA-15. Confinement of AB in nanoporous silica had a dramatic effect on H_2 release, lowering the release temperature by 20 °C, reaction enthalpy by 20 kJ mol^{-1}, and also the concentration of borazine impurity. To understand this behaviour we have investigated composites of AB in MCM-41 using a variety of methods including NMR spectroscopy (hyperpolarised ^{129}Xe, solid-state ^2H and ^{11}B), X-ray PDF analysis, anelastic spectroscopy, and Raman spectroscopy. We will discuss the results of these experimental studies. PNNL is operated by Battelle.

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Pseudocapacitor properties of nanostructured transition metal oxides

Bruce Dunn$^{(1)}$*, bdunn@ucla.edu, 3121 Engineering V, 410 Westwood Plaza, Los Angeles CA 900095, United States ; Veronica Augustyn*$^{(1)}$*; Tom Quickel*$^{(2)}$*; Sarah Tolbert*$^{(2)}$*. (1) Department of Materials Science and Engineering, University* *of California, Los Angeles, Los Angeles CA 900095, United States (2) Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles CA 900095, United States*

@font-face { font-family: "Courier New"; }@font-face { font-family: "MS Mincho"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 0.0001pt; font-size: 12pt; font-family: "Courier New"; }div.Section1 { page: Section1; } Capacitive energy storage is distinguished from other types of electrochemical energy storage by short charging times, long cycling life and the ability to deliver high power. A key limitation to this technology is its low energy density and for this reason there is considerable interest in exploring pseudocapacitive charge storage mechanisms. Our research has shown that nanostructured transition metal oxides are a very promising approach for achieving enhanced pseudocapacitance. Using TiO_2 as a model system, we find that pseudocapacitive contributions become increasingly important at crystallite sizes below 10 nm, leading to greater amounts of total stored charge without compromising kinetics. We have now extended these studies to mesoporous transition metal oxide films such as TiO_2, MoO_3 and Nb_2O_5. With these systems, there is the prospect of designing materials that possess both high energy and high power density.

COLL 397

Impact of nanoconfinement and additives on the hydrogen sorption in complex metal hydrides

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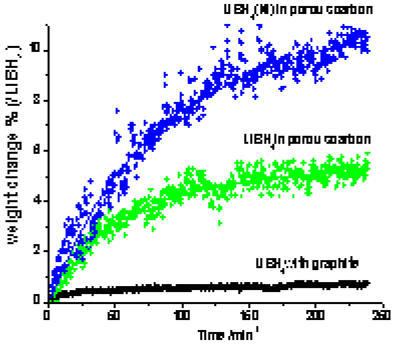
Complex metal hydrides are interesting hydrogen storage materials, but typically suffer from slow sorption kinetics and poor reversibility. We load $NaAlH_4$, $LiBH_4$ and $NaBH_4$ into mesoporous carbon scaffolds. The phase evolution during cycling is followed by techniques such as solid state NMR, EXAFS, HP-DSC.



Not only hydrogen sorption kinetics are changed by nanoconfinement, but also thermodynamical stability and decomposition pathway. Another important aspect is reversibility, as illustrated in the Figure 1 showing the H_2 uptake for $LiBH_4$/carbon at 320 °C, 40 bar H_2.

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Nanoparticulate RuO_2 dispersed on paper-like substrates for energy storage and conversion

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Ruthenium dioxide (RuO_2) is a technologically important electrocatalytic material used extensively in the chloralkali industry for chlorine production from brine and investigated for energy storage and conversion applications including water oxidation (hydrogen production), electrochemical capacitors, direct methanol fuel cell catalysts (when combined with platinum), and Li-ion insertion electrodes. The cost of RuO_2 precursors limits these and other applications, which has prompted development of highly dispersed, nanoscale forms of the oxide that maximize the number of catalytically active reaction sites while minimizing weight loading. In order to prepare highly-active, 3D electrode architectures with low loadings of RuO_2, we have developed a simple solution-based synthesis in which self-wired networks of RuO_2 deposit onto porous, paper-like substrates including commercially available SiO_2 filter papers ($RuO_2[SiO_2]$) or in-house fabricated carbon nanofoam papers (RuO_2[nanofoam]). On SiO_2 filter papers the RuO_2 forms a contiguous, nano“skin” of 2–3-nm RuO_2 particles wrapped around the individual fibers composing the paper. The RuO_2 network imparts high electronic conductivity and electrochemical activity to the otherwise insulating SiO_2 paper at only 5 wt% RuO_2. Because the oxide coating is virtually all surface (90% of the RuO_2 in a 2-nm particle is surface-sited) the utilization of this expensive catalyst is maximized. In contrast to the insulating, macroporous SiO_2 filter paper, the high-surface-area carbon nanofoams express a through-connected network of size-tunable pores (10s to 100s of nm) and high electronic conductivity, thus providing a pre-formed nanoarchitecture to distribute the nanoparticulate RuO_2. Here we present synthesis and characterization of the $RuO_2[SiO_2]$ and RuO_2[nanofoam] papers and their electrocatalytic activity with respect to energy storage and conversion applications.

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Hydrogen evolution from ammonia borane on the surface of nano-BN

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Ammonia borane based materials are very promising chemical hydrides that can be used for hydrogen storage applications. This paper will present recent results on the decomposition pathway of ammonia borane on the surface on nano-BN. The properties of these materials were investigated in correlation with the amount of additive. The characterization of these composites by XRD, RAMAN, 11B NMR, TG/DSC/MS, volumetric hydrogen measurements will be discussed.

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Using metal-organic frameworks to capture and store noble gases

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The combination of low natural abundance and very low reactivity makes the collection and measurement of noble gases quite challenging. Metal-organic frameworks (MOFs) with very high surface areas can adsorb noble gases in separation processes. With thousands of MOFs known, choosing the MOF best suited for noble gas capture is difficult. To guide synthetic work in this area, grand canonical Monte Carlo simulations were performed for an extended set of MOFs and five gases (argon, krypton, xenon, radon, and nitrogen). These MOFs were chosen to explore trends in gas adsorption as a function of pore geometry, uncoordinated metal sites, and linker functionalization. Henry's constants, adsorption energies, and adsorption isotherms were calculated and compared with experimental results. Additional MOF characteristics, including the percent free volume, specific surface area, and pore-limiting diameter, were also examined. Low-pressure gas adsorption is enhanced in MOFs with pore diameters equal to gas diameter. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a subsidiary

wholly owned of Lockheed Martin Corporation, for the U. S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

COLL 401

Catalysis by doped oxides

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We use computations and experiments to explore to what extent one can improve the catalytic activity of oxides by doping them. We classify the dopants in three classes: the cation in the oxide is replaced by a lower valence dopant, the cation is replaced by a higher valence dopant, or the oxygen is replaced by another anion. We perform calculations that explore the properties of each class and present experiments on methane combustion and partial oxidation and on CO_2 hydrogenation by doped oxides, which illustrate the concepts proposed by calculations.

COLL 402

Ab initio based modeling of perovskites for solid oxide fuel cell cathodes

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Our ability to improve perovskite solid oxide fuel cell (SOFC) cathode performance is limited by the complexity of the oxygen reduction reaction (ORR) and perovskite surface/bulk defect chemistry. Key challenges in understanding perovskites for SOFCs include defect interactions, changes in defect energetics near surfaces, and surface kinetics associated with the ORR. In this talk we will use *ab initio* techniques to model perovskite defect chemistry in the bulk and near the surface. Furthermore, we show how a descriptor approach can be used to predict oxygen reduction catalytic activity from *ab initio* energetics. This descriptor approach opens the door to *ab initio* design of more active SOFC cathode catalysts.

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Surface chemistry and activity of SOFC cathode materials as thin films

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Surface engineering of electrodes, e.g., infiltration of nanoscale electrocatalysts, holds promise for SOFC performance improvement. However, the surface properties of oxides in SOFC conditions are poorly understood. To build correlations between surface characteristics and properties, pulsed laser deposition was used to deposit thin films of $(La,Sr)MnO_{3\pm x}$ and $(La,Sr)(Co,Fe)O_{3-x}$ on perovskite and fluorite substrates. Correlations were made between surface chemistry and film structure and the electronic, electrochemical, and oxygen exchange properties. Using synchrotron XRF, cation segregation at was measured in operational SOFC conditions. The electronic properties of the surfaces of such films were measured using scanning tunneling spectroscopy at high temperatures, coupled with XPS, AES and EIS. Surface exchange was also measured using electrical conductivity relaxation and Kelvin probe spectroscopy. We will demonstrate that significant departures from bulk or ceramic values are observed for the surfaces of epitaxial films and will discuss their implications for SOFC improvement.

COLL 404

Role of band-filling, oxidation state, and strain on oxide reactivity

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The principles of reactivity for oxide surfaces are not as well understood as metal surfaces. We will discuss the role of band filling, strain and oxidation state on the reactivity of oxide surfaces, specifically on the adsorption energy of oxygen and the surface vacancy formation energy.

COLL 405

Brønsted-Evans-Polanyi relations for transition-metal oxides from density functional theory

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To be able to predict the reactivity of a given material towards a specific reaction it is of crucial importance to establish general rules, for example, Brønsted-Evans-Polanyi (BEP) relations for classes of materials. Such relations have been established from density functional theory (DFT) for transition metals and have been used in a successful way to predict volcano curves for several reactions. In this contribution, a computational screening study based on DFT is employed to probe the reactivity of a wide range of transition-metal oxides, including rutiles and perovskites. The focus it to (i) investigate whether BEP relations exist for dissociation of small molecules on oxides and (ii) whether these obey the universality rule found for metals, that is a reactant independent BEP relation. Using the versatile relations found for oxides as starting point, we discuss the suitability of oxides as catalysts as compared with metals.

COLL 406

Volcano relation for the Deacon process over transition-metal oxides

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Chlorine is one of the most important compounds for the chemical industry with a worldwide annual production of approximately 50 Mton. It can be produced from either hydrochloric acid or chlorine salts by electrochemical reduction. This process, however, is highly energy demanding and there has thus been growing interest in the heterogeneously catalyzed oxidation of HCl with oxygen using the so-called Deacon process. $4\ HCl + O_2 \rightarrow 2\ Cl_2 + 2\ H_2O$ ($\Delta H^{298K} = -114\ kJmol^{-1}$) Even though the Deacon process has been known for about 130 years, industrial production via this route was only established recently by Sumitomo Chemicals using a TiO_2 supported RuO_2 catalyst. **Results** We established an activity relation for the heterogeneous catalytic oxidation of HCl (Deacon process) over

rutile transition metal oxide catalysts by combining density functional theory calculations with microkinetic modeling. Linear energy relations for the elementary reaction steps have been obtained from the DFT calculations and were utilized to establish a one-dimensional descriptor for the catalytic activity. The desriptor that was employed here is the dissociative chemisorption energy of oxygen on the cus site of the rutile (110) surfaces. It was found that the commonly used RuO_2 catalyst is close to optimal, but that there could still be room for improvements. The analysis suggests that oxide surfaces which offer slightly weaker binding of oxygen should exhibit a superior activity to that of RuO_2. Having employed this one-dimensional descriptor a fast computational screening for materials with improved catalytic properties is now feasible.

COLL 407

Coupling classical electrodynamics with quantum mechanics for metal particle optical properties

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This talk will describe recent theory work in my group aimed at understanding plasmon excitation in silver and gold particles, and how this collective electron excitation influences single-electron excitation processes in molecules near the particles including absorption and surface enhanced Raman scattering. Two approaches will be considered: (1) a top-down theory in which nonlocal dielectric functions are included into classical electrodynamics, thereby incorporating quantum effects into the metal particle response, and (2) a bottom-up theory in which real-time time-dependent density functional theory for the molecule is combined with classical electrodynamics for the metal particle. Applications of these theories to plasmonic solar cells and to SERS for nanoparticle junctions will be described.

COLL 408

Adsorption and nucleation of metal clusters on Ru-supported graphene: A combined experimental and theoretical investigation

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Super-lattices of small metal clusters (SMCs) with narrow size distributions have been obtained recently on graphene moirés grown on single-crystal metal surfaces, notable examples including Ir_x/graphene/Ir(111) and Pt_x/graphene/Ru(0001)$^{1-3}$. To explore the possibility of developing different SMCs, we have deposited Co, Rh, Pd, Pt, and Au, on graphene/Ru(0001), and characterized the resulting materials using STM^{4}. At room temperature, well-dispersed SMCs are obtained with Rh and Pt, whereas Co, Pd, and Au coalesce into large islands. To understand the nucleation of SMC super-lattices, DFT-based calculations have been performed to study the adsorption diffusion of the monomers, dimers, and trimers of Rh and Au on graphene/Ru(0001) and the bonding interaction between the clusters, graphene, and the Ru substrate, to gain insight into why these metals cluster via different mechanisms on grapene/Ru(0001). Furthermore, we probe the chemical stability and reactivity of the Rh and Au clusters using CO as the probe molecule. □□ References: 1. A.T. N'Diaye, S. Bleikamp, P.J. Feibelman, T. Michely, Phys. Rev. Lett. 97, 2006, 215501 2. A.T. N'Diaye, T. Gerber, C. Busse, J. Myslivecek, J. Coraux, T. Michely, New J. Phys. 11 406, 2009, 103045 3. Y. Pan, M. Gao, L. Huang, F. Liu, H.-J. Gao, Appl. Phys. Lett. 95, 2009, 093106 4. Z. Zhou, F. Gao, D. W. Goodman, Surf. Sci., 604, 2010, L31

COLL 409

Computational studies on adsorption and diffusion of transition metal atoms on graphene and graphene/Ru(0001)

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Stable metal nanoparticles grown on metal-supported graphene have been observed experimentally. N'Diaye et al. reported the formation of Ir clusters on graphene/Ir(111) [1]. STM observation and analysis of five metal nanoclusters (Pt, Rh, Pd, Co, Au) formed on graphene/Ru(0001) was reported by Goodman and co-workers [2]. To understand the formation mechanism of metal nanoclusters on supported graphene, it is important to understand the adsorption and diffusion of single metal atoms on the moiré patterns formed by supported graphene. We studied the adsorption and diffusion of 18 different transition metals (Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, La, Hf, Ta, W, Re, Os, Ir, Pt, Au) on freestanding graphene and graphene/Ru(0001) using Density Functional Theory (DFT) with the generalized gradient approximation. The adsorption energies were calculated for the cases where transition metal atoms adsorbed to sites with high symmetry: top, bridge, and center. For graphene/Ru(0001), adsorption energies in hcp and fcc regions were investigated. Our results show a clear decreasing trend of adsorption energies along the periodic table. On

graphene/Ru(0001), the fcc region was predicted to be where the nucleation of metal nanoclusters occurs, which agrees with experimental observations. We also analyzed the potential energy surface (PES) of each metal on graphene and graphene/Ru(0001). Transition states and activation energies of single atom diffusion were determined from PES. We are currently in the process of using Monte Carlo techniques to study cluster formation on graphene/Ru(0001). These approaches will give insights into when “magic” cluster sizes exist for metal nanoparticles on metal-supported graphene. [1] A.T. N'Diaye, S. Bleikamp, P.J. Feibelman, T. Michely, Phys. Rev. Lett., 97 (2006) 4. [2] Z.H. Zhou, F. Gao, D.W. Goodman, Surf. Sci., 604 (2010) 1071-L1038.

COLL 410

Ab initio modelling of uracil molecules on gold surfaces

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The reactivity of gold nanoparticles can be investigated via adsorbing a model system to describe how molecular organic films can modify the properties of the substrate, and, eventually, control the functionalities transferred to the surface. Here, we report on our investigation of the interactions between the RNA nucleobase, uracil, immobilized on two major gold surfaces found in gold nanoparticles, Au(100) and Au(111). We will show results from calculations by plane-wave Density Functional Theory methods, including a correction for the dispersive forces, to describe the interplay between the lateral non-covalent intermolecular interactions and the transverse reaction to the substrate.

COLL 411

Structure/property mapping of colloidal titania photocatalysts

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The design of optimal nanoparticle photocatalysts requires a detailed understanding of how fundamental materials parameters relate to photoactivity; a field often referred to as structure/property mapping. Unfortunately, in the case of nanomaterials, the structure may vary in response to changes in their chemical and thermal surroundings, so it becomes necessary to generate sets of structure/property maps for all possible permutations, polymorphs and environmental conditions. An efficient way of doing this is to use mathematical modeling and computer simulations to rapidly sample the structure space. This study traces the development of a nanoscale phase diagram for anatase and

rutile nanocrystals using thermodynamic cartography and density functional theory, to predict the most probable structure as a function of size, shape, temperature and surface chemistry. These structural predictions are then used as a basis for structure/property mapping of photocatalytic activity, by overlaying the population density of cationic sites on the active surface facets.

COLL 412

Theoretical investigation of the size-dependent structures and properties of cadmium selenide nanoclusters

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It is known from mass spectroscopy experiments that among small $(CdSe)_n$ nanoclusters the formation of particular "magic size" clusters is particularly favored. In search of the most stable geometry of small $(CdSe)_n$ nanoclusters, we explored various ways to construct a series of cut-from-bulk, fullerenic cage, and stuffed cage types of materials at each size up to n=36. These structures, together with additional configurations obtained from biased *ab initio* Monte Carlo basin hopping calculations, were relaxed at the hybrid density functional theory level. Results show that the preferred geometry of $(CdSe)_n$ nanoclusters changes from ring to cage, then to stuffed cage types as the size evolves in the studied region. The crossover to the cut-from-bulk configuration as the most stable geometry is expected to occur in even larger size regions. A correlation is drawn between the stability of the nanoclusters and their structural, electronic and optical properties at various sizes. An interpretation is also proposed for the selective formation of magic size nanoclusters.

COLL 413

Controlling biotinylation of microgels and modeling streptavidin binding

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Poly(N-isopropylacrylamide-covinylacetic) microgels are water swollen particles with a corona of carboxyl groups. Biotinylation of the microgels by amino-PEG derivative of biotin or biotin hydrazide were compared. The biotinylated microgels

are a platform for bioactive water-based ink. The colloidal stability of the biotinylated microgels was preserved. Streptavidin binding was measured as a function of biotin density and the results were interpreted with a new model that predicts the minimum local density of biotins required to capture a streptavidin. The streptavidin content versus biotin content results fell on a master curve with maximum biotin coverage of 0.11 mg of bound streptavidin per mg of biotinylated microgel. Exclusion experiments showed that streptavidin was too large to penetrate the crosslinked microgel structure thus the conjugated streptavidin was restricted to the microgel surface.

COLL 414

Environmental photochemical reactions of single-walled carbon nanotubes (SWNTs) in aqueous suspensions

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We have investigated photochemical production of reactive oxygen species (ROS) in aqueous suspensions of commercial preparations of carboxylic acid functionalized SWNTs, polyethylene glycol functionalized SWNTs, and unmodified (i.e., pristine or unfunctionalized) SWNTs. Using FFA, a tetrazolium salt, and *p*-chlorobenzoic acid as molecular probes for singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\cdot -}$), and hydroxyl radial (·OH), respectively, photoproduction of all three reactive oxygen species occurred in aqueous suspensions of both types of functionalized nanotubes, but not to any significant degree in aqueous suspensions of unfunctionalized SWNTs (containing sodium dodecylsulfate {SDS}) over the time period of our experiments. SDS was added to facilitate disaggregation and dispersion of unfunctionalized nanotubes. Defects in the fullerene surface caused by functionalization may facilitate ROS production, as well as differences in amorphous carbon and metal impurity content within the different SWNT preparations. These results suggest that functionalization, even with moieties that do not contain sunlight-active chromophores, and/or surface defects strongly influence the environmental photoreactivity of SWNTs, and potentially the environmental persistence of carbon nanotubes in general.

COLL 415

Influence of nanoparticle surface chemistry on NOM sorption and colloidal stabilization: Particle properties matter!

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By combining sorption and aggregation experiments with surface characterization, the influence that surface oxygen plays in regulating the colloidal stability of multi-walled carbon nanotubes (MWCNTs) in the presence of NOM has been elucidated. Sorption studies revealed that NOM adsorption decreased systematically as a function of increasing oxygen concentration, while the influence of pH and ionic strength on NOM sorption also increasing as the degree of MWCNT surface oxidation increased. In the presence of NOM, the colloidal stability of MWCNTs was greatly enhanced due to steric stabilization. However, the effectiveness of NOM in stabilizing MWCNT particles was greatest for MWCNTs with lower oxygen concentrations, due to greater NOM sorption. Consequently, at environmentally relevant NOM concentrations the colloidal stability of MWCNTs was inversely dependent on its oxygen concentration. These results highlight the fact that a particle's intrinsic surface properties will play an important role in determining its stability in the natural environment.

COLL 416

Accelerated ageing of silver nanoparticles in the laboratory and comparison to material aged in environmental mesocosms

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Most studies regarding the fate and impacts of silver nanoparticles (AgNPs) (e.g. transport and toxicity) use the pristine starting material rather than environmentally aged AgNPs which will have different physicochemical properties than the pristine materials. The objectives of this study are to determine accelerated aging protocols for AgNPs that can mimic the speciation of AgNPs exposed to environmental media. Ag NPs are aged in the laboratory under various environmental conditions and characterized with regard to attributes that will influence environmental behavior and effects. Synchrotron X-rays are used to detect the oxidation products of AgNPs, including the highly insoluble acanthite (Ag_2S), in environments like waste water treatment plant by-products, and soils, among others. Comparisons between laboratory aged materials and real environmental samples and a discussion of the parameters that dictate environmental speciation will be presented.

COLL 417

Physico-chemical characterization of the UV-induced transformations of silver nanoparticle suspensions

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The effect of ultraviolet (UV) light (300 nm) on the physico-chemical properties and toxicity of silver nanoparticle (AgNPs) suspensions has been studied. The size dependent kinetics of the UV-induced transformations was explored using four different diameters of AgNPs. The rate of the AgNPs' photo-induced degradation was determined through the use of UV-vis spectroscopy. Changes in the AgNPs' chemical speciation, size and aggregation state were further explored with a combination of dynamic light scattering, atomic force microscopy and x-ray photoelectron spectroscopy. Acute toxicity of irradiated and non-irradiated AgNP suspensions was evaluated in both freshwater and saltwater invertebrates (daphnia magna and artemia, respectively) to determine the presence/absence of a change in toxicity.

COLL 418

Fate, biological effects, and analysis of single walled carbon nanotubes in the aquatic environment

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Because of their unique physicochemical properties, concerns have emerged over potential adverse effects of nanomaterials such as SWNTs in the environment. Recent work in our laboratories has focused on the analysis, environmental fate, and effects of these contaminants in aquatic systems. SWNTs are stabilized in colloidal solutions by coating with natural organic matter, but this stability is highly dependent on solution ionic strength. Increasing ionic strength leads to aggregation of SWNTs as well as deposition of these materials to natural particulates. In addition, SWNTs adsorb organic contaminants strongly from aqueous solutions. These results indicate that SWNT will associate with aquatic sediments, where they may become important in modulating fate of molecular contaminants. SWNTs themselves are relatively non-toxic to benthic

deposit feeders, but their manufacturing byproducts may cause effects. SWNTs are not bioaccumulated from ingested sediments by benthic organisms; however, organisms ingesting SWNT-associated organic contaminants accumulate these compounds in their tissues.

COLL 419

Zinc oxide nanoparticle aggregation and dissolution in a model surface water: The role of organic matter and clay minerals

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In this study, the fate of zinc oxide nanoparticles (ZnO NPs) was investigated in a model surface water (pH: 6, 7, and 8); short term (<4 hrs) aggregation and dissolution was monitored in the presence of Suwannee River Natural dissolved or colloidal matter (DOM or COM respectively). ZnO NP point of zero charge (ZPC) was determined to be ~pH 9, and the greatest aggregation was observed at pH 8. DOM tended to enhance particle aggregation, while colloidal OM (COM) tended to suppress aggregation, possibly because is further reduced the particle zeta potential. Dissolution was greatest at pH 6 and 7 (~70%). At pH 8, dissolution was minimal, however OM mediated re-adsorption was observed. Progressive centrifugation was the better method for size resolved Zn distribution. This research is currently being expanded to investigate ZnO NP interactions with clay mineral colloids in the presence of DOM or COM.

COLL 420

Organic acid adsorption on engineered metal and metal oxide nanoparticles in aqueous suspensions

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Nanomaterials industry, an anticipated enterprise of $1 trillion by the year 2015 has resulted in the large scale production and wide variety of applications of engineered metal and metal oxide nanoparticles. Because surface chemistry of nanoparticles plays a key role in the fate of these materials, the primary focus of this study has been given on both the details of the surface chemistry of organic acid on metal and metal oxide nanoparticles; TiO_2, CeO_2 and Cu, including measurements of surface coverage and speciation, and its impact on nanoparticle behavior in aqueous environment. Using macroscopic and molecular-based probes, organic acid adsorption and nanoparticle interactions are measured with quantitative solution phase adsorption measurements, ATR-FTIR spectroscopy, dynamic light scattering techniques and zeta-potential measurements as a function of solution pH. Furthermore particle dissolution and aggregation behavior has been studied extensively along with HRTEM to obtain detailed information on these processes. The results of this study are needed to better understand the distribution and bioavailability of metal and metal oxide engineered nanoparticles in natural aqueous environments.

COLL 421

Dissolution and transformation of mesoporous silicas in aqueous environment: Kinetics and implications

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Owing to their extremely high surface area and unique pore structure, mesoporous silica materials (e.g., SBA15 and MCM41) have been used in applications such as adsorbents for toxic metals and organic contaminants, as catalyst supports in hydrogen peroxide-based oxidative water treatment as well as in organic synthesis processes. Despite the widespread use of these nanomaterials, little is known about their stability and transformation in aqueous systems. Given their high surface area and poor crystallinity, as well as the relatively high solubility of amorphous silica, it is expected that SBA15 and MCM41 will dissolve resulting in the release of aqueous silica species that could alter catalyst activity. To test this hypothesis, a series of experiments was performed to evaluate the rate of SBA15 and MCM41 dissolution in aqueous solutions with different pH values and the impact of silica species on catalyst activity. The catalytic activity of the metal-containing mesoporous silica was evaluated by measuring rates of H_2O_2 loss through the heterogeneous Fenton reaction. Results of these studies reveal substantial changes in catalyst structure that decrease the rate of H_2O_2 decomposition. These findings provide insights into the activity of mesoporous silica catalysts as well as the fate of these nanomaterials in the environment.

COLL 422

Biodegradation of ^{14}C-labeled multi-walled carbon nanotubes

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Understanding possible environmental transformation of carbon nanotubes is critical for their life-circle environmental risk analysis. Recent studies have discovered biotic degradations of fullerols and single-walled carbon nanotubes (SWNTs), but there has not been a report on microbial degradation of MWNTs. We in our on-going study identified an enrichment culture that is capable of mineralizing ^{14}C-MWNTs into $^{14}CO_2$. Our initial study indicates that the mechanism involved in MWNT degradation seems to differ from that has been reported for fullerols and SWNTs. The microorganisms responsible for MWNTs degradation may not be fungi, but, a consortium of bacteria, and the peroxidases that were found responsible for SWNT and fullerol degradation were absent in the MWNT-degrading culture. We are currently conducting a systematic study to identify and characterize the microorganisms that are responsible for degrading MWNTs and the biochemical pathways that are involved in MWNT metabolism.

COLL 423

Mechanisms responsible for the initial aggregation of metal oxide NPs in water

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Nanoparticles have been observed to form large aggregates at the scale of hundreds of nanometer immediately after being dispersed in water. This phenomenon has been observed in different media, with or without dispersing agents and for a number of metal oxides. It is intriguing that this occurs for neither C_{60} nor hematite. Understanding this phenomenon is importance since it affects accurate prediction of environmental transport and toxicity of nanoparticles. Sonication and heat were applied to TiO_2 suspension to investigate the mechanism. Both stimuli disintegrated the aggregate, but neither was able to break the aggregates down to primary size. The aggregate size interestingly raised back after the stimuli were removed. These results suggest the coexistence of a strong/irreversible attraction and a weak/reversible attraction between TiO_2 nanoparticles. DLVO calculation accounted for fractal nature of the aggregates revealed that the switch from primary minimum aggregation to secondary minimum aggregation could explain the observation.

COLL 424

Continuum models for biomembrane dynamics

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Simulation of biomembranes and model membrane systems over length and time scales relevant to cellular biology is not currently feasible with Molecular Dynamics or related atomically-detailed methods. Barring an unforeseen revolution in the computer industry, this situation will not change for several decades. Two aspects of membrane dynamics will be discussed: out-of-plane membrane undulations and in-plane flow/diffusion in inhomogeneous membrane systems. Both problems are treated within the context of continuum models, which allow access to length and time scales up to and beyond the micron and second regimes, using simple numerical methods. A number of effects relevant to the motion of integral membrane proteins as well as the dynamics of phase separation and domain fluctuations in multi-component lipid bilayers will be presented.

COLL 425

Phase separation in supported lipid bilayers on xerogels and microfabricated ridges

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Lipid bilayers, deposited onto nano-porous, microfabricated or atomically flat substrates, offer many advantages with respect to construction of devices and study of biological membrane processes. We demonstrate that the characteristics of these substrates (e.g. curvature) can strongly influence the phase behavior of a mixed lipid bilayer. First, we show that high curvature (r ~ 50 nm) in a silica xerogel layer can be used to induce lipid demixing or intrabilayer transport over large areas. Second, we use large-angle microfabricated ridges (Θ ~ 179°) to align freely moving lipid domains in a multilayer system.

COLL 426

Formation and structure of lipid microdomains: Roles of thermodynamics, non-equilibrium processes, and hydrodynamics

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@font-face { font-family: "Arial"; }@font-face { font-family: "CMR10"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 6pt 0in 0.0001pt; text-align: justify; font-size: 12pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } Compositional lipid microdomains ("lipid rafts") in lipid membranes are believed to be important components of many cellular processes. The biophysical mechanisms by which cells regulate the size, lifetime, and spatial localization of these domains are rather poorly understood at the moment. In this talk, I will first critically review existing theories for raft formation. Then, I will highlight a theoretical method we have developed to experimentally falsify these models. Finally, I will discuss the role of membrane and solvent hydrodynamics on lipid microdomain formation kinetics in synthetic membranes.

COLL 427

Multiscale simulation of membrane remodeling by proteins

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Cellular responses and (mis)function are determined by processes on mesoscopic time and length scales, relative to atomic dimensions. However, these same processes may be disrupted by molecular-level interactions — this is the defining feature of a multiscale problem. Membrane remodelling by specialized protein domains (e.g., the BAR domain, a long banana-shaped homodimer) is one such example. The amphiphysin and endophilin N-BAR domains (the BAR domain plus an N-terminal amphipathic helix) are thought to play a key role in clathrin-mediated endocytosis. We have developed and applied a "bottom-up" multiscale approach consisting of atomistic molecular dynamics (MD), coarse-grained (CG), and mesoscopic simulations to explore membrane remodelling at various length and timescales, making connection wherever possible with electron microscopy results obtained by the Unger group at Northwestern. The N-BAR domain is shown to be a protein module whose shape, electrostatic properties, and amphipathic helices transform liposomes into a wide variety of topologies at mesoscopic levels, in agreement with experimental results. The atomistic-level MD simulations demonstrate the local membrane bending ability of both amphiphysin and endophilin N-BAR domains, while the CG simulations, which are systematically constructed from the atomistic MD data, allow much larger scale phenomena to be studied.

COLL 428

Single channel recording as a functional assay for non-ionic polymer – biomembrane interactions

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Biological membranes are complex dynamic cell structures which serve as shields from the external environment. The use of amphiphilic block copolymers as agents to modify cell membrane structure and function has been an area of increasing research interest. Of particular interest has been the use of commercially available amphiphilic triblock copolymers of PEO_n-PPO_m-PEO_n, so-called Pluronics or Poloxamers. Numerous investigations have explored their use in a wide range of biomedical applications, including modifiers in drug delivery, in-situ generated implants, synthetic chaperones, barriers against bacterial adsorption, neuroprotective and restorative agents, and soft tissue injury treatments (including stroke and electrical / thermal burns). In our prior work, we have identified specific polymer architectures among this family of triblock copolymers that seal defects or that form anti-microbial barriers on cell surfaces. In this work, we describe the application of single-channel recording as a functional assay to evaluate how the association of selected non-ionic polymers alters lipid bilayer permeability. Specifically, ion current changes are monitored for polymers of varying architectures and are shown to yield insights on polymer-induced biomembrane structure and function.

COLL 429

Diffusion of protein clusters on cell membranes

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I will present the concepts, mathematics, and experimental data regarding clustered diffusion of proteins on a cell membrane with cortical cytoskeleton barriers. Oligomerization is known to slow diffusion, but that slowing can be difficult to represent properly and depends heavily on the model of barrier-crossing. Clustering around a multivalent extracellular ligand, however, is a different process with fundamentally different consequences for diffusion. Further, it can be represented in a way that is both mathematically similar in almost any model of barrier-crossing and potentially capable of distinguishing between those models.

COLL 430

Determination of electron density profiles and area-per-lipid from molecular dynamics simulations of large undulating lipid bilayers

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The simple, traditional method for extracting electron density and other transmembrane profiles from molecular dynamics simulations of lipid bilayers fails for large bilayer systems because it assumes a flat reference surface that does not take into account the long wavelength undulations that develop. We have developed a novel set of methods to characterize these undulations and extract the underlying profiles in the large systems. Our approach first obtains an undulation reference surface for each frame in the simulation and subsequently isolates the long wavelength undulations by filtering out the intrinsic short wavelength modes. We then describe two methods to obtain the appropriate profiles from the undulating reference surface. All combinations of methods give similar results for the electron density profiles. We have also developed a set of methods that use the undulation reference surface to determine the true area per lipid, which due to undulations, is larger than the xy-projected area that is commonly reported from simulations.

COLL 431

Aqueous nanocarbon dispersions for electronic and energy applications

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@font-face { font-family: "Cambria"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 10pt; font-size: 12pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } Microemulsion polymerization was used to prepare nanolatexes using a reactive ionic liquid surfactant (ILBr) and methylmethacrylate (MMA). Such nanolatexes have high affinity for nanocarbon and graphene surfaces and can be used to stabilize various forms of nanocarbon in an aqueous environment. Such dispersions are expected to lead to primary fuel feeds for carbon-based fuel cells. Introductory results are demonstrated for dispersing single wall carbon nanotubes, multiwall carbon nanotubes, and hydrothermally produced nanocarbon at practical concentrations of 1-11% by weight in aqueous dispersion! We present optical criteria useful for establishing complete exfoliation. Electrical conductivity, and thermal conductivity properties are presented and discussed.

COLL 432

Electrocatalytic CO_2 conversion over copper oxide nanoparticles

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The sequestration and utilization of carbon dioxide is currently an extremely important, albeit challenging goal. The electrochemical conversion of CO_2 over copper has been widely investigated, but many questions remain concerning the reaction mechanism and influence of the catalyst surface. We have found that Cu_2O and CuO nanoparticles stabilized with an organic capping layer function as catalysts for the electrochemical conversion of CO_2 into CO and HCOOH. We show that nano-copper oxide electrocatalysts promote CO_2 conversion more efficiently than bulk copper and copper oxide catalysts by a factor of 10^2-10^4. Electron microscopy, electrochemistry, a variety of spectroscopic techniques and chromatography have been used to investigate the catalyst structure, nature of the active sites, and product distributions. Our data suggests that a high density of unique reactive sites on the nanoparticle surface promotes the conversion of CO_2 into CO and HCCOH over the evolution of H_2.

COLL 433

Nanostructured titania composites: Photocatalysts for energy applications

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Photoinduced reactions on titania has received considerable attention due to their potential applications in dye sensitized solar cells, photosplitting of water to hydrogen, photo catalytic self-cleaning surfaces etc. The photocatalytic reduction reactions in which conversion of carbon dioxide to hydrocarbons using titania nanostructures are an important and emerging area of inquiry with respect to solar fuel production. The objective of the present work is to explore the effect of different types of titania nanostrucutres such as nanotube, nanorods, nanosheets and composites with graphene and carbon nanotubes for the photocatalytic reduction of carbon dioxide to fuel. It was found that photoactivity is highly dependent on the morphology and the mass ratio of the composites. Further,

these composites are effectively used for photoreduction under visible light, which leads to the possible application of these catalysts for solar energy conversion to fuel.

COLL 434

Nearfield scanning optical microscopy characterization of arrays of rare earth based nanocrystals

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Rare earth based nanocrystals are of great interest due to their unique photoluminescent characteristic of upconversion; absorption of near infrared radiation then emission of visible photons. Therefore, these materials provide excellent resolution for increasing the efficiency of solar cells by utilizing the 20% infrared and near infrared radiation of the sun. Using a home-constructed nearfield scanning optical microscope (NSOM), we studied the size, geometry, and surface functionality in correlation with the photoluminescent spectra of individual $NaYF_4$:Yb,Er nanocrystals and arrays of $NaYF_4$:Yb,Er nanocrystals generated by particle lithography. In contrast to prior aperture and apertureless NSOM, our new design exploits the photoluminescence of Si_3N_4 atomic force microscopy tips under laser excitation to delineate between near-field and far-field signals. These initial investigations provide new insights into the structure-spectroscopy relationship of engineered rare earth nanomaterials to guide the optimization of these nanomaterials in photovoltaic applications.

COLL 435

Nanoclay-based electrolyte membranes for fuel cell and battery applications

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Reducing costs and increasing power densities of fuel cell and battery technologies requires improved material utilization. We are studying ionically conductive layered nanoclays (smectites and layered double hydroxides) as possible building blocks for fuel cell and battery structures. The goal of this technique is to locate the ionic conductor in close-proximity to the fuel cell catalyst or battery electrode material by tailoring the structure at the nano-level. As part of this work, we have been developing nanoclay-based electrolyte membranes. Techniques used in the creation of these membranes include TMOS CVD and solvent-based polymer-clay hybrid casting. Conductivities measured by AC impedance spectroscopy for sodium-exchanged membranes have been observed in the 10^{-3} to 10^{-2} S/cm range at room temperature. Additional characterization of the membrane nanostructure has been performed using SEM/EDS and XRD, among other tools. Synthesis methods and characterization results for these nanoclay-based membranes will be reported.

COLL 436

Synthesis, colloidal crystallization and solar cell application of monodisperse ZnO quantum dots

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ZnO quantum dots (QDs) with a nearly uniform particle size of 5 nm have been synthesized, purified and dispersed in organic solvent. Colloidal crystal of monodisperse ZnO QDs, which is transparent to visible light and blocks UV-light as bulk material, has been prepared via interparticle potential tuning without using surfactants as a stabilizer. Mesoporous thin film of ZnO QDs has also been fabricated as a seed layer for hydrothermal growth of ZnO nanorod arrays, of which the interstitial space can be efficiently filled by dispersed ZnO QDs. For solar cell application, ZnO nanoparticles were conjugated with dye molecules (Ruthenium 535-bisTBA) to enhance light absorption and a p-type semiconducting polymer film was deposited on the top of the nanorod arrays to replenish lost electrons in dye molecules. Compared with the device using ZnO nanorods alone, the efficiency of the hybrid structure of ZnO nanorods and QDs has been significantly improved.

COLL 437

Hot-injection growth of semiconductor nanocrystals onto substrate-bound oxide films for light-harvesting applications

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We report a simple strategy for growing lead chalcogenide nanocrystals directly on polycrystalline TiO_2 films via hot-injection routes. The method is enabled by introducing a thin layer of substrate-bound oxide into the reaction flask prior to the injection of organometallic precursors, which leads to the formation of PbS(Se, Te)/TiO_2 nano-composites exhibiting a fully inorganic interface between NC and TiO_2 domains. Fabricated composite films can be harnessed as working electrodes in several solar cell architectures, leading to power conversion efficiencies in excess of 1%. From the synthetic standpoint, the present method extends the traditional synthesis of semiconductor nanocrystals in solutions, allowing a preferential growth of nanocrystallites onto a suitable substrate, which is placed into the reaction flask prior to the injection of precursors. The resulting substrate-bound nanocrystals exhibit a narrow distribution of sizes, characteristic to hot-injection methods, and form near-epitaxial relationships with the host material, leading to a high-quality NC/oxide interface.

COLL 438

Investigations of the surface chemistry and colloidal stability of nickel oxide particles in non-aqueous media

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Direct write methods of printing NiO-based inks have recently been explored as low-cost ways to generate the anode interlayer of solid oxide fuel cells (SOFCs). Reliable printing of the NiO-based catalytic layers of the solid oxide fuel cell requires formulation of colloidal NiO dispersions that display long term stability. In the present work, diffuse reflectance infrared spectroscopy and thermal analysis are used to characterize the surface water and hydroxyl species present on the NiO powder. The type of water and hydroxyl species detected on the NiO powder are then correlated with the zeta potential and sedimentation velocity of NiO inks prepared through dispersion of the NiO powder with acidic and basic dispersants in non-aqueous media. It is found that surface hydroxyls influence the stability of the NiO particles in non-aqueous media.

COLL 439

Developing titania/ferroelectric heterostructures for solar photolysis

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A series of photochemical reactions have been conducted on thin titania films supported by ferroelectric substrates ($BaTiO_3$ and $BiFeO_3$) with a wide range of orientations. For all of the orientations and both phases of titania, the thinnest films have reactivities equal to or greater than the bulk-like films, suggesting that the charge separating characteristics of the substrate have the potential to increase the reactivity of titania. When titania is supported by the narrower bandgap ferroelectric $BiFeO_3$, photochemical reactions on the titania surface can be stimulated by visible light with an energy smaller than titania's bandgap. Finally, the efficacy of the dipolar field effect is demonstrated by measurements of hydrogen evolution rates from a composite catalyst comprised of $BaTiO_3$ particles coated with mesoporous titania. The rate of hydrogen evolution from the composite catalyst exceeds the rate of hydrogen evolution from the $BaTiO_3$ or the mesoporous titania alone.

COLL 440

Photocatalytic properties of nanostructured TiO_2 containing materials for splitting of H_2O

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Photocatalysis involves phenomena occurring at high time resolutions under unique conditions. Studies probing these time scales under relevant *in situ* conditions will lead to improved photocatalysts. Thus, catalysts containing 1-60 wt% TiO_2/SiO_2 were dehydrated under flowing 10% O_2 at 400 °C. Using a pulsed laser for excitation and a gated detector with picosecond time resolution, the lifetime of excited states of the samples was determined *in situ* at room temperature. H_2 production was monitored by gas chromatography for the water splitting reaction in a UV-irradiated reactor. The excitation lifetime measurements indicate that lower wt% samples have longer excited lifetimes, which correlates with increased specific H_2 production rates. The water splitting reaction's intermediates and product formation were monitored using attenuated total

reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy during transient UV irradiation. Hydrogen titanate nanotubes were also prepared using a hydrothermal method. It was shown with *in situ* Raman spectroscopic characterization that post synthesis thermal treatment transforms the titanate nanotubes to TiO_2 (anatase) nanotubes. The photocatalytic water splitting activity of the TiO_2 nanotubes were also determined. This presentation will develop the relationship between the titania structure-photoactivity properties for the different TiO_2 nanodomains (supported TiO_2/SiO_2 and unsupported TiO_2 nanotubes).

COLL 441

Visible light semiconductor photocatalysis enhanced by Ag nanoparticle plasmon resonance

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The efficient conversion of solar energy into useful chemical energy, for example through processes such as water splitting and CO_2 reduction, is of critical importance for the development of sustainable, long-term solutions to society's energy problems. These and other photochemical processes require the development of novel photo-catalysts that can efficiently make use of the solar spectrum. TiO_2 has been studied extensively as a promising photo-catalyst because it is abundant, cheap and stable under reaction conditions. TiO_2 absorbs ultraviolet (UV) light, creating electron/hole (e/h) pairs, which can perform redox half-reactions for a range of photochemical processes. However, UV accounts for only a small portion of the solar spectrum. Shifting the band gap of TiO_2 to lower energy (e.g., by adding various dopants) allows for absorption in the visible spectrum, which represents ~50% of the solar spectrum. The result is a material that shows photo-catalytic activity upon illumination with visible light. However, the absorption efficiency of the doped materials in the visible region is inherently low, which leads to low visible photo-reaction rates. In this contribution we show that the photocatalytic activity of visible light active nitrogen-doped TiO_2 can be significantly enhanced by the addition of optically active Ag nanostructures of targeted size and shape to form composite metal/semiconductor photocatalysts. We will discuss the underlying mechanims governing the observed phenomena. The ability to predictably tune the Ag SPR by controlling particle shape and size allows for the rational design of optimized metal/semiconductor composite photocatalysts and photo-electro-catalysts wherein the overlap of the metal nanostructure SPR, semiconductor band gap, and energy of the light source is maximized.

COLL 442

Fundamental structure-photoactivity relationships of advanced photocatalysts for splitting of H_2O

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Several advanced photocatalytic systems (i.e. TaON, GaN:ZnO, $NaTaO_3$:La) have recently been shown to catalyze the water splitting reaction. The photoactivity of these bulk materials is greatly enhanced by loading precious metal co-catalysts such as NiO and/or RuO_2 onto their surfaces. The bulk molecular and electronic structures of these photocatalysts were characterized using optical spectroscopic methods (Raman, IR, and UV-vis). Their corresponding surface composition information as well as the effect of the co-catalyst loading was obtained with Low Energy Ion Scattering (LEIS) and X-ray Photoelectron Spectroscopy (XPS). Steady-state attenuated total reflection (ATR) FT-IR will be used to determine the nature of surface species during UV irradiation to elucidate further insights into the fundamental structure-photoactivity relationships of these novel catalytic materials.

COLL 443

Electrocatalysis on manganese oxide surfaces: Oxygen reduction and water oxidation

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Catalytic conversions between water and molecular oxygen are key processes in nature as well as in commercial devices such as fuel cells and water electrolyzers. The development of effective electrocatalyst materials for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) remain major technical challenges. We have recently developed a nanostructured manganese oxide surface capable of catalyzing both reactions at relatively low overpotentials; the bi-functional activity of this surface in executing the ORR and the OER is comparable to that of the best known precious metal catalysts: ruthenium, iridium and platinum. This paper will focus on three general topics: (1) our recent work in understanding the surface chemistry of this catalyst and the nature of its excellent bi-functional activity, (2) the effects of crystal structure and stoichiometry on both reactions, and (3) how electrochemically

induced phase changes of the surface of manganese oxides impact the catalytic processes involved.

COLL 444

Structural changes accompanying interfacial charge transfer between dye/TiO_2 nanoparticles studied by transient X-ray absorption spectroscopy

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Photo-induced interfacial electron transfer between the dye and semiconductor nanocrystalline has important applications in solar cells, quantum dot devices and photocatalytic hydrogen generation. Chemical and electronic properties of the species undergoing photoinduce electron transfer are determined largely by their static and transient structures of the ground and excited states. Directly visualizing these structures is necessary for molecular/material designs for targeted functions, therefore, realizing the rational designs of solar cells. X-ray transient absorption or laser-initiated, time-resolved X-ray absorption spectroscopy (XTA or LITR-XAS) has been used to probe the photo-induced structural changes at dye-nanoparticle interface. Two examples will be presented: $Ru(dcbpy)_2(NCS)_2$ and $Os(dcbpy)_2(CN)_2$ adsorbed to TiO_2 nanoparticle surface. The photoexcited Ru and Os complexes inject electrons into the conduction band of TiO_2, leading to an interfacial charge separated state, $(TiO_2)_n^-/(dye)^+$. The electronic configuration as well as the internuclear distance changes of metal complexes in the charge separation state has been observed. These measurements demonstrate a significant potential of using LITR-XAS to study the interfacial phenomena at surface of nonmaterial in solar fuel generation.

COLL 445

Quantum simulations based design and modeling of nano-scale composite cathode materials for high energy density Li-ion battery

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High rate and high energy density lithium ion batteries (LIB) constitute a major requirement for plug-in-hybrid (PHEV) and electric (EV) automotive, and smart-grid related energy storage applications. Year-to-year electrochemical performance improvements in Li-ion batteries are typically limited to within 3-4% unless new electrode materials, chemistries and improvements in them are introduced rapidly. Nanoexa has developed a patent pending *ab-initio* density functional theory (DFT) level quantum simulations based battery materials database and design technology platform for new LIB electrode materials compositions and morphologies much faster than what is feasible through the current empirical experimental methods. The acceleration of technology innovation and development includes not only the quantum simulated database and materials composition design software but also the experimentally synthesized, characterized, and validated nano-scale compositions and composites for specific capacity, voltage, volume-change on charge and discharge, relative safety and cycling, and electrochemical discharge curves. This talk will describe the basic underlying technology with simulated results and comparison with experimental data, followed by a focus on materials synthesis for nano-scale morphology control and the link to coin-cell level discharge curves for Li-(NCM)-Oxide type composite cathode materials

COLL 446

Computational studies of carbon-onions for electrochemical capacitor applications

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Electrochemical capacitors or supercapacitors have high power and energy density, bridging the gap between conventional batteries and electrolytic capacitors. Nano-onion-like carbon structures have [1] energies/capacitances several orders higher than conventional cells, making them the fastest growing technology in this area. In spite of novel experimental breakthroughs, a good understanding of their structure and relationship to their superior electrical properties remains elusive. We study formation and temperature stability of nano-carbon-onions using reactive force-fields [2] which include long-range interactions, absent in previous simulations. Characterization of the final structure suggests that there are more sp^2-bonded carbons in simulations with long-range interactions, which in turn help increase the temperature stability range in agreement with experiments. [1] D. Pech *et.al*, Nature Nanotechnology **5**, 651 (2010) [2] Adri C. T. van Duin *et.al*, J. Phys. Chem. A **105**, 9396 (2001) Work

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COLL 447

Molecular dynamics studies of heat transfer at the interface of model diamond {111} nanosurfaces: Effects of pressure and interfacial chemical composition

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Bulk resistance to heat flow can play an important role in the design and manufacture of nanograined diamond composite materials. A high density of grain boundaries exists in fully compacted nanocomposites. This equates to a very large number of interfaces per unit volume. At lower temperatures, where thermal conductivity is dominated by phonon conductivity, the interfacial geometry controls heat transfer, reducing it significantly. This work reports on molecular dynamics simulations that were performed using the valence force, OPLS-AA, and AIREBO potentials. The simulations studied the effects of pressure and interfacial chemical composition on heat transfer across the interface of diamond {111} nanosurfaces. Heat transfer occurred with exponential kinetics and a rate constant that increased with pressure. This improved understanding of controlling factors for heat transfer can assist in tailoring of compositions and synthesis conditions for the next-generation nanodiamond products, such as PDC cutters, bearings, and coatings.

COLL 448

Predicted site dependence of the binding energies of functional groups on diamond nanoparticles: A new route for multifunctionalization?

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The facile surface chemistry of diamond has made nanodiamonds attractive for many applications in the materials and bio-medical sciences. To better understand and predict covalent bonding of surface species to diamond nanoparticles, we have been using an analytic force field and a semi-empirical electronic method to calculate binding energies for different functional groups

chemically attached to hydrogen-terminated diamond nanoparticles. The calculations predict that in general functional groups are more strongly bound to apex sites, followed by edge and then terrace sites. The differences in binding energies between the different sites are attributed to geometric effects that reduce steric repulsion between the functional groups and surface hydrogen for the apex and edge sites compared to the terrace sites. This variation in binding energy suggests different thermal lifetimes of these sites, and the possibility of using thermal cycling in different plasma environments to create nanoparticles with spatially heterogeneous chemical activity.

COLL 449

Non-covalent surface modification of carbon nanoparticles: A molecular dynamics study

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Carbon nanoparticles are an attractive option for a variety of applications due to their nanometer sizes, distinct shapes, strong mechanical features, high surface reactivity, robust thermal conductivity, and electronic properties. However, the high surface reactivity can also lead to agglomeration of the nanoparticles, which has an adverse effect on bulk properties. Surface modifications of carbon nanoparticles help to control dispersion, solubility and interfacial phenomena. While the covalent engineering of a nanoparticle can control the dispersion, it can also reduce its electrical and mechanical properties. Therefore, noncovalent surface engineering is the best route to improve dispersion and preserve the nanoparticle properties. We will discuss molecular dynamics simulations that were performed to investigate noncovalent interactions as a function of polymer composition and processing conditions such as solvent, and how they can be used to optimize the desired properties of the material; these results will be correlated with experimental efforts.

COLL 450

Adhesion of nanoparticles

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I will present a new model of nanoparticle adhesion which explicitly takes into account the change in the nanoparticle surface energy. Using combination of the

molecular dynamics simulations and theoretical calculations it will be shown that the deformation of the adsorbed nanoparticles is a function of the dimensionless parameter $b=g(\mathrm{GR}^{)-2/3}\ \mathrm{W}^{-1/3}$, where *G* is the particle shear modulus, R is the initial particle radius, *g* is the polymer interfacial energy and *W* is the particle work of adhesion. In the case of small values of the parameter $b<0.1$, which is usually the case for strongly cross-linked large nanoparticles, the particle deformation can be described in the framework of the classical Johnson, Kendall, and Roberts (JKR) theory. However, there is a significant deviation from the classical JKR theory in the case of the weakly cross-linked nanoparticles that experience large shape deformations upon particle adhesion. In this case the interfacial energy of the nanoparticle plays an important role controlling nanoparticle deformation. A new model of the nanoparticle adhesion is in a very good agreement with the simulation results and provides a new universal scaling relationship for nanoparticle deformation as a function of the system parameters.

COLL 451

On the interaction of equally charged nanoparticles in presence of a size-asymmetric salt

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The electrical double layer of macroions in solution plays a determinant role in the macroscopic properties of charged solutions such as stability, flocculation and zeta potential values, which are relevant in science and technological applications. Molecular simulations where colloids, ions and solvent particles (water) are considered explicitly are in general prohibitively expensive computationally, specially if long-ranged electrostatic interactions are included properly. Thus, a coarse-grained scheme in which hydration effects can be taken into account implicitly, by using different effective radii for the ions in a continuous solvent medium is particularly suitable. Thus, in this work are shown some theoretical and simulation results displaying interesting phenomena such as surface charge amplification and charge reversal for an infinite diluted colloidal solution, with special emphasis in the potential of mean force between two identical spherical charged nanoparticles, immersed in a monovalent size-asymmetric electrolyte in aqueous medium.

COLL 452

Theory and modeling of ordering of nanoparticles in dispersion

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We use atomistic simulation to study the orientation of nonpolar nanoparticles suspended in water and subject to an electric field. Because of the molecular level effects we describe, the torque exerted on the nanoparticle exceeds continuum-based estimates by about a factor of two. We suggest a novel mechanism to orient nanoparticles by an electric field even when particles have no net charges and their permittivity is the same as of the medium. Coupling to the field is accomplished through solvent-mediated interaction. For nanoscale particles in water, we find the response to the applied field to be sufficiently fast that this mechanism is likely to be relevant for biological processes, for the design of novel nanostructures and sensors, and development of nanoengineering methods.

COLL 453

Surface confinement of ligands on nanoparticles studied by SERS and ^{1}H solid state NMR spectroscopy

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As most polyfunctional nanoparticles are prepared by ligand exchange reaction, the detailed knowledge of molecular dynamics for the adsorbed monolayer on nanopaticles will make it possible to fine-tune the surface properties of such particles. Here we report the studies of mobility of ligands on Au nanoparticle by the use of ^{1}H solid state NMR and surface enhanced Raman scattering (SERS) spectroscopies. We find that surface interaction relates not only to the terminal functional groups, but also to the entire chains. Moreover, by comparison of the ligand exchanges of a number of surfactants, we find that surface confinement on the surface species plays an important role on the competitive adsorption. These results indicated that the surface confinement of ligand can be one of the important factors which influences the reaction activities on nanoparticles.

COLL 454

Desorption of metals from metal oxide nanoparticles: Equilibrium and kinetics studies

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In our previous work, we have show that metal oxide nanoparticles can be used to remove metals from water. In this work, the desorption of metals (Pb, Cd, Ni, Cu, Zn) from hematite (Fe_2O_3) and titanium dioxide (TiO_2) nanoparticles was studied, looking at both equilibrium and kinetic effects. The equilibrium studies were conducted with metals being adsorbed at pH 8.0 for 24 hrs, and then desorbed in metal-free solutions for three cycles (24 hrs each) at pH 4.0, 6.0, and 8.0. Desorption was pH dependent, for example, Pb onto TiO_2, 86.9% was desorbed at pH 4.0, 47.1% desorbed at pH 6.0, and 0% desorbed at pH 8.0 at the end of three cycles. The result showed that desorption of metals in different pH solutions had the following trends: pH 4.0 > pH 6.0 > pH 8.0 and the 1st cycle > 2nd cycle > 3rd cycle. This indicates that lowering the pH can enhance desorption of metals from the nanoparticles. The desorption kinetic studies for each metal were conducted at pH 4.0, 6.0 and 8.0 like the equilibrium studies except only for 2 hrs. The desorption process can be separated into two periods: rapid desorbing period (1-15 min) and slow desorbing period (15-120 min). Kinetic models were used to fit the data and each desorption period. Understanding desorption will aid in developing methods for spent nanoparticles regeneration, which would make the method more cost-effective and environmental-friendly.

COLL 455

Influence of multi-wall carbon nanotube surface oxidation on hydroxyl radical formation during ozonation

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We have previously shown that multi-walled carbon nanotubes (MWCNTs) can be used to increase hydroxyl radical (•OH) production during ozonation, oftentimes to levels comparable or exceeding traditional ozone-based advanced oxidation processes (AOPs). Here, we explore the relationship between MWCNT surface oxidation and •OH production during ozonation. Chemical routes for MWCNT functionalization were used that systematically vary surface oxygen content, and the ability of these functionalized materials to generate •OH was subsequently determined in batch ozonation experiments with *para*-chlorobenzoic acid (*p*-CBA) as a radical probe. Complementary surface analysis with X-ray photoelectron spectroscopy (XPS) combined with chemical

derivatization was used to correlate •OH production not only to total MWCNT surface oxygen content, but also to the concentration of specific functional groups (hydroxyl, carbonyl and carboxylic acid groups) resulting from oxidation. Results to date show that •OH production increases with MWCNT surface oxidation. Changes in MWCNT surface chemistry from oxidation appear responsible for this enhanced reactivity, as evidence suggests it cannot be explained solely by the increased dispersivity of oxidized MWCNTs in aqueous suspensions.

COLL 456

Environmental applications of electrochemically-active filtration: Multiwalled carbon nanotube membrane

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Nanotechnology has the potential to solve many environmental issues including the development of new and more effective water treatment technologies. Here, we present the design and evaluation of an ELectrochemically-active Filter (ELF) composed of a dense mat of randomly-oriented multiwalled carbon nanotubes (MWNT) that form a macroporous conductive membrane. The MWNT-ELF is shown to be effective for the removal and inactivation of both bacteria and viruses. The electrochemical inactivation is observed to be a function of applied potential, and at potentials > 2 V; zero active microorganisms are detected in the effluent. The MWNT-ELF is also shown to be effective for the electrochemically-mediated adsorption, desorption, and oxidation of various aqueous chemicals. Environmental applications of ELF will be discussed.

COLL 457

Application of engineered, nanocrystalline iron oxides (nMAG) for uranium analysis in aqueous samples

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Work described demonstrates an optimization and application of engineered, monodispersed, nanoscale iron oxide particles (termed nMAG) as concentration/seperating agents for uranium analysis in aqueous samples. Taking advantage of favorable sorption chemistries, sorbed uranyl species can reach >25% by weight associated with nanoscale magnetite particles (12 nm), which are surface stabilized with an oleic acid bilayer. Because these materials exhibit strong, permanent magnetic properties, they can be selectively removed from complex samples using magnetic fields resulting in high concentration factors. Furthermore, as these materials are surface stabilized and monodispersed, homogenous thin films can be formed minimizing the self-absorption/blocking of α-particle emission from uranium isotopes. Taken together, engineered material features enhance uranyl detection (via α-counting) by over 1000 times when compared to a commercial available, aggregated, "nanoscale" iron oxide.

COLL 458

Sorption of metals to hematite nanoparticles: Competitive and temperature effects

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The presence of metals in natural waters is becoming an emerging environmental and public health concern. The use of iron and iron oxide nanoparticles has been identified as a potential remediation technique in removing metals from water. This study investigates the sorption properties of Zn(II), Cu(II), Cd(II), and Pb(II) to nano-hematite in single- and binary-adsorbate systems. Competitive sorption was evaluated in 1L batch binary-metal systems with 0.05g/L nano-hematite at pH 8.0 and pH 6.0. Results indicate that the presence of a secondary metal can affect the sorption process depending upon the molar ratios, such as increased or reduced adsorption. Affects of temperature were also evaluated to determine thermodynamic properties of the sorption process. Understanding the thermodynamic properties can give insight to determine if the sorption process is a physical, chemical or ion exchange reaction. Batch adsorption experiments were conducted for single-metal systems at 15°C, 30°C, and 45°C with 0.05g/L nano-hematite at pH 6.0. Initial results show that Pb and Cu adsorption to nano-hematite is an endothermic, and a physical adsorption process; however, it is only spontaneous at higher temperatures. Thermodynamic, isotherm, and kinetic results will also be presented.

COLL 459

Core-shell structure of nanoscale zero-valent iron (nZVI): Implications for arsenic sequestration

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The core-shell structure of nanoscale zero-valent iron (nZVI) has been examined using a variety of characterization tools. Knowledge about the structure and chemical nature of the nanoparticles yields valuable insights into the reactivity of the nanoparticles in environmental remediation systems. One good example concerns the removal of arsenic species with nZVI, where recent investigations show that the reactions between nZVI and arsenite species (As(III)) reflect a dual redox functionality of nZVI enabled by the core-shell structure. Based on solution phase analysis and surface chemistry characterization with high-resolution X-ray photoelectron spectroscopy (HR-XPS), we observed that arsenite was rapidly sequestered from water and underwent a set of redox reactions within nZVI, resulting in multiple arsenic valence states (i.e., As(0), As(III) and As(V)) present in the solid phase. Time-dependent and multiline XPS analyses indicate that As(III) was oxidized to As(V) at the surface of the oxide shell on a time scale of minutes. The As(V) formed slowly reverted to As(III) when sufficient nZVI was present. Meanwhile, gradual infiltration of arsenite through the oxide layer and the formation of elemental arsenic (As(0)) at the metal iron/oxide shell interface were observed. The relative extents of these reactions and the resultant arsenic speciation and spatial distributions in the nanoparticles vary with experimental conditions and the composition of nZVI. The findings presented here suggest that nZVI possesses more complex functionality than bulk Fe(0) or iron oxides. The reactivity imparted by the core-shell structure may translate to attributes favorable for *in situ* arsenic remediation.

COLL 460

Aging characteristics and reacitivities of atmospherically stable nanoscale zero-valent iron particles

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Atmospherically stable NZVI (Nanoscale Zero-Valent Iron) particles were prepared by controlled air contact procedures. The NZVI particles were resistant to rapid aerial oxidation when they were exposed to air. Synthesized(Fe^{BH}) and commercial(Fe^{H2}, Toda RNIP) NZVI particles were modified by the controlled air contact procedures that utilized different types of oxygen (ambient oxygen from air, oxygen from purified air, purified oxygen) and different amounts of oxygen.. Instrumental analyses using TEM, XRD, XPS, and XANES revealed different morphologies and mineralogies of each NZVI particle. Synthesized NZVI particles showed much higher reactivity and reduction capacity than the commercial one for nitrate removal. Results of re-activation experiments for each NZVI particles indicate that each NZVI particle may go through different passivation processes when they react with nitrate. Core/shell models for each NZVI particles when they are aged by air, water, and contaminants were proposed based on the results.

COLL 461

Toxicity of reduced iron nanoparticles to *Escherichia coli*: Implications for groundwater remediation

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In situ, passive technologies for remediating contaminated groundwater offer potential economic and environmental advantages over *ex situ*, active extraction methods. Most *in situ* technologies involve emplacing reactive materials in the path of a contaminant plume with the goal of transforming or sequestering contaminants in the reactive zone. Approaches to effectively create the reactive zones, known as permeable reactive barriers (PRBs), have typically involved the use of reduced iron materials, such as zero valent iron (ZVI), but more recently nanoparticle forms of these materials have been investigated. Other reactive reduced iron minerals have also been studied, such as ferrous sulfide, as they naturally form as nanoparticles. Although incorporating nanoparticles into PRBs is potentially beneficial due to their high reactive surface area, questions regarding their release risk and toxicity have not yet been answered. The toxicity of nano ZVI and FeS particles to model bacteria, *E. coli*, is reported in this research.

COLL 462

Atomic force microscopy characterization of normal and cancer prostate cells

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The cell mechanical properties in terms of the parameters adhesion, Young's, and dilation modulus and stiffness values for the prostate cell lines RWPE-1 (benign), RWPE-2 (nonmetastatic), DU145 (moderately metastatic from brain metastasis), and PC3 (highly metastatic from bone metastasis) have been determined by atomic force microscopy (AFM). A large number of force-distance approach curves were obtained to discern differences between the cell lines and histograms for each parameter were generated. Analysis of histograms indicated a log-normal distribution from which the average, median, and standard deviation values for each parameter were obtained. Significant differences in all the parameters were observed between the cell lines as indicated by statistical analysis of the data. In general it was found that as cells transitioned from a normal to a highly metastatic phenotype they had higher elasticity and stiffness, and greater ability to dilate and bend. The mechanical properties of the prostate cells could be rationalized based on the glassy materials model. The densities of cell surface molecules and average interaction distances of these molecules and AFM cantilever tip were also determined. A long and short interaction distance with the cantilever tip at small and large indentations was observed. These interaction distances increased from normal to highly metastatic cells with a decrease in the corresponding molecular densities. Taken together these results indicate that the response of normal and cancer cells to nanoindentation forces are significantly different reflecting their phenotypes.

COLL 463

Ergosterol and temperature modulated changes in dynamic and static properties of DPPC membranes

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Using molecular dynamics (MD) and atomic force microscopy (AFM) we examine how ergosterol affects 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC) lipid bilayers above and below the T_m (41ºC). Ergosterol is the predominant sterol in fermenting microorganisms such as yeast and is present in concentrations from 10 to 25 mol%. We performed atomistic simulations of DPPC at 5 temperatures (15-50ºC) and 4 ergosterol concentrations (0-30 mol%). These ergosterol concentrations and temperatures cover a broad range of macroscopic phases including the gel ($L_{\beta'}$), liquid ordered (L_O), and liquid disordered (L_α). Our analysis focuses on lateral pressure profiles and time-dependent correlation functions. Parallel to simulations, we use AFM of similar supported lipid bilayers to investigate membranes at the microscopic level. The high resolution AFM images allow observation of micron-sized phase separation between the L_{β}' and L_O phases. Our results provide new insights to sterol-lipid interactions and how they affect dynamic and mechanical properties of lipid membranes.

COLL 464

Effect of curvature array on lipid phase behavior

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Biomembranes present different types of curvatures that can induce specific lateral organization of the lipids. The influence of curvature has motivated studies to investigate the relationship between membrane curvature and lateral organization. We investigate the effects of curvature on the lipid miscibility of a ternary lipid mixture containing 1,2–dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-distearoyl-sn-gycero-3-phophocholine (DPPC) and cholesterol, which is spin-coated onto a homogenous Poly(methyl methacrylate) support with curved array features. We show that variation of the composition below and above the miscibility point along with curvature (10µm – 100nm hemispherical arrays) of the support causes changes in the phase behavior allowing the analysis of the relation between the curvature and the location of the domains. The characterization of the system is done using fluorescence and atomic force microscopy. This homogeneous surface allows examination of large-scale demixing which resembles the scale of demixing of the plasma membrane.

COLL 465

Quartz crystal microbalance with dissipation monitoring (QCM-D) studies and comparison of alamethicin and chrysophsin-3 action on cell membranes

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Antimicrobial peptides (AMPs) are naturally occurring molecules that protect against infection by attaching to bacterial surfaces, disturbing the membrane, and causing them to lyse. However, the active mechanism behind the membrane

destabilization is not well understood. Once attached, AMPs are thought to align themselves along the surface and form micelles from the lipid membrane or insert themselves into the membrane and form a pore. Quartz crystal microbalance with dissipation monitoring (QCM-D) was used to determine the action of the AMPs alamethicin and chrysophsin-3 on a phosphatidylcholine (PC) lipid bilayer attached to a sensor. The interaction between the PC membrane and alamethicin, which is known to form pores in cell membranes, was observed real-time. The exposure of 0.25 - 4 μM chrysophsin-3 solutions to a PC membrane resulted in a pore formation mechanism. More mass addition was also observed at lower overtones, indicating more chrysophsin-3 attachment at the membrane surface.

COLL 466

Confocal imaging to quantify carboxylic acid passive transport across lipid membranes

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The passive transport of low-molecular-weight carboxylic acids across cell membranes has been widely studied, but studies over the decades have yielded wildly varying membrane permeability values. We have used confocal microscopy to image the transport of carboxylic acids with different carbon chain lengths into and out of a giant unilamellar lipid vesicle (GUV). The pH-sensitive dye fluorescein-dextran was encapsulated in the GUV to trace the transport of acid. The GUV was immobilized on the surface of a microfluidic channel by biotin-avidin binding, allowing the rapid exchange of buffer solution. Confocal microscopy allows the temporal development of the entire concentration field to be tracked with great precision. A finite difference model was used to obtain permeability values for the observed transport process. The results showed that as the acid chain length increases, permeability increases. In contrast to other recent results, this trend corresponds to increasing acid hydrophobicity.

COLL 467

Cholesterol concentration modulates the mechanical properties of cellular plasma membranes

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Cochlear outer hair cells exhibit electrically induced movements known as electromotility, a membrane-based phenomenon which allows for the sensitivity and frequency-resolving capability of mammalian hearing. Membrane cholesterol content modulates the membrane charge movement and electromotility in outer hair cells. Using human embryonic kidney cells, as model cells, we have examined the effects of membrane cholesterol on viscoelastic properties of the plasma membrane. Optical tweezers were used to form plasma membrane nanotubes (tethers) from cells treated with 3 and 5 mM concentrations of water soluble cholesterol, and methyl-beta-cyclodextrin for cholesterol enrichment and cholesterol depletion experiments, respectively. We performed tether pulling experiments with single and multi-speed protocols in order to obtain time-resolved membrane tether force profiles. The tether formation force, tether formation energy, tether equilibrium force and effective membrane viscosity of the plasma membrane were quantified and correlated to the changes in the membrane cholesterol level. Tether formation force increased as membrane cholesterol was decreased. Higher tether equilibrium force and membrane stiffness were also associated with cholesterol depleted cell membranes. Tether effective viscosities were determined using multi-speed pulls, and increased in cholesterol enriched cells.

COLL 468

Characterizing the interactions between lyso-lipids and supported lipid bilayers using microcantilevers

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The amphipathic nature of surfactants causes morphological changes to supported lipid membranes. We used microcantilevers as sensors for probing the interactions between lyso-lipids and SLBs. In particular, we investigate the effects of three zwitterionic surfactants, lyso-lipids, of different aliphatic chain lengths (12, 14 and 16 hydrocarbons, or lysoPC 12:0, 14:0 and 16:0) on supported lipid membranes. The microcantilevers are coated with a 5 nm supported lipid bilayers (SLBs). By monitoring the change in the deflection of the microcantilevers, real-time free energy changes in the coated SLBs upon the addition of lyso-lipids can be detected. The results show that, for bulk concentrations of lysoPCs less than CMC, all three lysoPCs bind to the SLBs, leading to compressive stresses on the microcantilevers. For bulk concentration of respective lysoPCs greater than CMC, lysoPC 12:0 and 14:0 start to solubilize the SLBs, while lysoPC 16:0 does not. The application of microcantilevers to study the insertion of amphipathic molecules, such as surfactants, membrane-

active peptides and drugs, into supported lipid bilayers can add additional insights on the interactions between small molecules and lipid membranes.

COLL 469

Improving the efficiency and stability of PbX (X=S, Se) nanocrystal solar cells using Atomic Layer Deposition Infilling

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PbX (X = S, Se) nanocrystal thin film solar cells are receiving increasing attention due to their potential to achieve >100% external quantum efficiency (EQE) via multiple exciton generation and enhanced cell voltages from the collection of hot carriers. However, PbX NC based devices are prone to oxidation and their performance typically decreases quickly in air. We show that PbSe NC films infilled with Al_2O_3 via low-temperature atomic layer deposition (ALD) are robust against oxidation and other mechanisms of degradation in air. Schottky-type solar cells constructed from these infilled films are stable in air for at least months. In addition, ALD was used to fabricate thin films of ZnO for inverted PbS/ZnO heterojunction solar cells. Growth temperature and pulse and purge times were varied to investigate the effect of ZnO film properties on the performance of the PbS/ZnO devices.

COLL 470

Efficient charge separation on interfaces of photovoltaic nanomaterials: Ab initio results

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Type-II core-shell quantum dots provide unique control over spatial distribution of carriers. The band offset value of the comprising materials establishes the direction of the energy transfer and enables optical transition energies beyond band gap restricions: The type-II quantum dots can emit at lower energies than the band gaps of comprising materials. The artificial solar energy harvesting technology involves photoinduced Interface charge separation on the interfaces of different materials: a photoabsorber (X), an electron conductor (E), and a hole conductor (H). The energies of valence band maximum, conduction band

minimum, and band-gap for these materials must satisfy certain conditions that provide a frequency-selective electron-hole-pair creation in X, and an efficient charge transport of en electron from X to E and a hole from X to H materials respectively.We study interfaces of a wide range of photovoltaic materials with various ionization energies, electron affinities, Fermi energies, crystalline structure. Specifically, we focus on photoexcited electron transfer in interfaces of II-VI group semiconductors of wurtzite crystal symmetry in form of thin film interfaces and quantum dots. An interface of CdS/ZnSe materials has a potential for the primary event of charge separation represented by the following reaction (CdS)(ZnSe) + hw -> (CdS)*(ZnSe) -> (CdS)-(ZnSe)+, where symbols *, -, + stand for excited, negatively, and positively charged states of a material, respectively. Theoretical calculations based on density matrix method provide charge transfer dynamics, photocurrent, photovoltage, and open circuit I-V curve for ground and photoexcited state.

COLL 471

Geometric packing, nanoparticle interaction & the origins of optical redshifts in PbSe quantum dot solids

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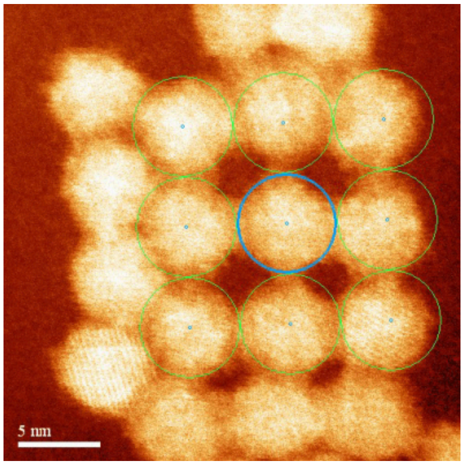
Understanding how semiconductor quantum dots (QD) assemble, couple and behave electronically in a QD solid is an open challenge with implications for both electronic and optoelectronic applications. We expand on this premise by manipulating the inter-QD distance in two-dimensional (2D) and three-dimensional (3D) arrays through the use of alkanedithiol linking molecules. With decreasing length of linking molecules, optical absorption spectroscopy of the QD assembly shows a tunable redshift in the 1st and 2nd exciton peak positions, but with minimal broadening of the peak width (<5%). HRSEM reveals a transition in packing configuration from hcp with C18 (oleic acid), C8 and C6 alkanedithiols to a mixed hcp/cubic/disordered packing motif when C5-C2 or no linking molecules are used. A majority of the tunable reshifts of the QD solids is attributed to polarization (dielectric effects) and a minority to resonant dipole interactions. This conclusion is confirmed in experiments with QD solids composed of mixed sizes. Optical broadening is only observed with extended hydrazine treatment wherein the gradual removal of capping molecules leads to decreased interparticle distance and aggregation of the QDs. Our work demonstrates two significant regime changes in QD-QD interaction: (1) a

transition from hcp with longer chain alkanedithiols to mixed hexagonal/cubic/disordered geometries, and (2) a transition in inter-QD coupling from a polarization/resonant dipole regime at inter-QD distances of 1.2-2.8 nm to electronic coupling at distances less than 1 nm.



COLL 472

Plasmonic nanostructures for enhanced absorption in ultrathin film solar cells

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Many potential solar cell materials suffer from a tradeoff with device thickness: while thinner cells have improved collection, higher open circuit voltages, and reduced costs, they also show reduced photocurrents due to decreased absorption. Plasmonic nanoparticles integrated into the back metal contact of an ultrathin film solar cell can enhance absorption via controlled coupling of incident free space optical modes into localized resonant modes and propagating guided wave modes. We have fabricated ultrathin film amorphous Si cells that exhibit a 10% enhancement in photocurrent over randomly textured back reflectors, and an improvement of 50% over flat back reflectors. Conformal deposition with both top and backside texturing leads to broadband enhancement over the solar spectrum. Electromagnetic modeling confirms the observations, and is used to optimize the pattern. Coupling to waveguide modes is confirmed via angle resolved photocurrent measurements. We will discuss the role of nanoparticle shape, size, and arrangement on the photocurrent, as well as applications to other materials.

COLL 473

Thermoelectric power factor enhancement by modulation doping

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We introduce the concept of modulation doping to improve the thermoelectric power factor in nanocomposite materials by incorporating heavily doped nanograins into an intrinsic host matrix. A significant increase of electrical conductivity in nanostructured p-type Si/SiGe composites by modulation doping is observed in comparison to that of uniform nanostructured p-type SiGe alloys leading to enhanced power factor. The enhancement is due to an increase in carrier mobility caused by the reduction of ionized impurity scattering of holes in the matrix. We were able to explain the experimental data by averaging over individual single grains. With no fitting parameters, the experimental data on thermal and electrical conductivity are reproduced within less than 20% error. Based on the modelling, the criteria of choosing the right materials for modulation doping are discussed. Further exploration of this approach in combination with strategies to reduce the thermal conductivity can lead to enhancement of the figure-of-merit by choosing appropriate materials and engineering the Fermi level.

COLL 474

Nanocrystal based solar cells

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COLL 475

Fabricating porous nanoarchitectures for energy storage

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Several recent articles have contrasting views on the importance of pore geometry in electrochemical double-layer capacitor materials. We hypothesize that the pore geometry of macroporous carbon nanoarchitectures does not affect the magnitude of capacitance or the rate of charge transport within pore networks. To address this question, we fabricate and compare the electrochemical double-layer capacitances of carbon inverse opal fabrics and carbon nanofoam electrodes—two nanomaterials that are otherwise similar except for the periodicity of their pore networks. Both materials are relatively new classes of nanomaterials that have greater mechanical flexibility and electronic conductivity than conventional carbon aerogels and carbon inverse opal monoliths. We will compare the physical and electrochemical properties of both carbon nanoarchitectures. Preliminary evidence based on cyclic voltammetry and impedance spectroscopy indicates that both electrode nanoarchitectures discharge similar amounts of capacitance and enable ionic charge to transport throughout macropore networks in similar durations of time.

COLL 476

Nanowire electrodeposition for advanced photovoltaics

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According to the Department of Energy's "Basic Research Needs for Solar Energy Utilization" report, there are a number of fundamental scientific issues that need to be addressed for nanostructure based solar cells, including: a. Control of nanoarchitecture b. Light harvesting c. Control of charge separation and recombination d. Control of charge carrier transport to the contacts Here, I will describe how lithographically patterned nanowire electrodeposition (LPNE) can address these issues by discussing the synthesis of high-density semiconductor nanowire arrays, as well as their optical and electronic properties. This talk consists of three parts. Part 1 presents a brief overview of how LPNE, essentially the combination of photolithography and electrodeposition, can be used as a general method to prepare high-density nanowire arrays. Part 2 demonstrates this method specifically for CIS/CdS core-shell nanowire arrays by discussing the electrodeposition of the nanowire arrays as well as the physical and chemical properties of the resulting nanowires. Finally, part 3 presents the optoelectronic properties of the resulting nanowire arrays and their potential application as solar cells.

COLL 477

Preparation of supported vanadium oxide catalysts: The role of surface molecular chemistry on oxide surface structure

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Despite widespread importance in catalysis, the active and selective sites of supported vanadia catalysts are not well understood. A complete structural elucidation requires isolation and characterization of specific vanadium oxide surface species, the preparation of which presents a significant synthetic challenge. In this work we utilize the structural uniformity inherent to organometallic complexes for the preparation of supported vanadium oxide catalysts. The resulting catalysts are characterized by UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS), X-ray absorption spectroscopy (XAS), UV-Raman spectroscopy, and H_2-temperature programmed reduction (H_2-TPR). Significant structural and reactivity differences are observed in catalysts prepared from different organometallic precursors, indicating that the chemical nature of surface vanadia can be significantly influenced by the nuclearity of the precursor used for grafting.

COLL 478

Surface of ZnO during hydrothermal growth

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The many applications of aspect-ratio-controlled ZnO crystals has stimulated the study of hydrothermal growth of ZnO in the presence of small molecules. The small molecules are thought to selectively control the growth of different faces. Although many have demonstrated the control of growth using small molecules, the specifics of the growth mechanism, and the microscopic influence of molecules has not been well characterised. We show that, under hydrothermal conditions, the growth of ZnO proceeds via ε-$Zn(OH)_2$, and that growth of ε-$Zn(OH)_2$ is rate limiting. Therefore, the action of small molecules is on ε-$Zn(OH)_2$. Further, we demonstrate the specific bonding of carboxylic acids, and amines to particular faces.

COLL 479

Adsorption and mobility of trimethylacetic acid molecules on TiO_2(110)

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The adsorption states, bonding configurations, and diffusion of trimethylacetic acid (TMAA) molecules on the reduced TiO_2(110) surface at RT have been examined at the atomic level by a combination of the scanning tunneling microscopy (STM), x-rays photoelectron spectroscopy (XPS) and density functional theory (DFT). Upon TMAA dissociation through deprotonation, two distinctly different types of stable chemisorption configurations of the carboxylate group (TMA) have been identified accordingly to their position and appearance in STM images. In configuration *A*, two carboxylate O atoms bonds to two Ti^{4+} cations, while in configuration *B* one O atom fills the bridging oxygen vacancy (V_O) with the other O bounded at an adjacent regular Ti^{4+} site. Calculated adsorption energies for the configurations *A* and *B* are comparable at 1.28 and 1.36 eV, respectively. DFT results also show that TMA may rotate at RT about its O atom that filled the V_O (in configuration *B*), with a rotation barrier of ~0.65 eV. Both the observation of the constant initial sticking coefficient and preference for TMAA molecules to dissociate at selective sites indicate that TMAA adsorption is mediated by a mobile precursor state. Several possible molecular (physisorbed) states of TMAA have indeed been identified by DFT, all being a highly mobile at RT. In contrast, the TMA diffusion in chemisorbed (dissociative) state is a very slow with calculated barrier of 1.09 eV for diffusion along the Ti row. [1] Lyubinetsky, I.; Yu, Z.Q.; Henderson, M.A.; *J. Phys. Chem. C* **2007**, *111*, 4342. [2] Lyubinetsky, I. ; Deskins, N. A.; Du, Y.; Vestergaard, E.K.; Kim, D.J.; Dupuis, M.; *Phys. Chem. Chem. Phys.* **2010**, *12*, 5986.

COLL 480

In situ X-ray and theoretical studies of a model heterogeneous catalyst: WO_x/α-Fe_2O_3

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Statistically averaging surface-sensitive X-ray techniques are combined with first-principles calculations to elucidate the surface morphology of a model oxide-supported heterogeneous catalyst, tungsten oxide (WO_x) on hematite (α-Fe_2O_3). Atomically flat α-Fe_2O_3 (0001) single crystals were coated with sub-monolayer WO_x by atomic layer deposition (ALD). *In situ* synchrotron X-ray standing wave (XSW) imaging with X-ray fluorescence (XRF) was employed to determine W position relative to bulk-like cation lattice sites under reducing and oxidizing chemical conditions. X-ray absorption fine structure (XAFS) reveals details of W coordination, bond length, and chemical state on WOx-coated hematite single crystals and nanopowders. Synchrotron characterization results are compared with morphologies predicted by density functional theory (DFT) simulations. Bond lengths, ionic charges, and densities of states are calculated for clean WO_x/α-Fe_2O_3 surfaces as well as for adsorbed H_2O and CO. Excited-state self-consistent field (SCF) calculations are used to model X-ray photoelectron spectroscopy (XPS) results.

COLL 481

Metal nanoparticles dispersed on CeOx/TiO2(110) surfaces: High WGS activity and the nature of the mixed-metal oxide at the nanometer level

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CeOx nanoparticles deposited on TiO2(110) have an unusual coordination mode. Scanning tunneling microscopy and density-functional calculations point to the presence of Ce2O3 dimers, which form diagonal arrays. The titania substrate imposes on the ceria nanoparticles nontypical coordination modes, enhancing their chemical reactivity. This phenomenon leads to a larger dispersion of supported metal nanoparticles (M) Au, Cu, Pt) and makes possible the direct participation of the oxide in catalytic reactions. The M/CeOx/TiO2(110) surfaces display an extremely high catalytic activity for the water-gas shift reaction that follows the sequence Au/CeOx/TiO2(110) < Cu/CeOx/TiO2(110) < Pt/CeOx/TiO2(110). For low coverages of Cu and CeOx, Cu/CeOx/TiO2(110) is 8-12 times more active than Cu(111) or Cu/ZnO industrial catalysts. In the M/CeOx/TiO2(110) systems, there is a strong coupling of the chemical properties of the admetal and the mixed-metal oxide: The adsorption and dissociation of water take place on the oxide, CO adsorbs on the admetal nanoparticles, and all subsequent reaction steps occur at the oxide-admetal interface. The high catalytic activity of the M/CeOx/TiO2(110) surfaces reflects the unique properties of the mixed-metal oxide at the nanometer level.

COLL 482

Role of hydroxyl groups in the reactivity and photoluminescence of metal oxide nanoparticles and surfaces

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Nanoparticulate metal oxides are being used for various applications, including gas sensors and organic photovoltaics. Surface science techniques, including X-ray photoelectron spectroscopy, have been used to investigate the role that adsorbed hydroxyl groups play in affecting the reactivity of metal oxide single crystals and nanoparticles to gases such as sulfur dioxide, methanol, and methanethiol. Metal oxides studied include titanium dioxide, zinc oxide, cerium oxide and tungsten oxide. Adsorbate-induced changes in the photoluminescence of the nanoparticles have been correlated with reactive gas uptake, with dramatic changes observed. The role of hydroxyl groups in ultraviolet (UV) light-induced changes in hydrophilicity of titanium dioxide surfaces is also discussed, and experiments are reported in which UV irradiation through a photomask has been used to pattern subsequently deposited materials.

COLL 483

In-situ spectroscopic study of the oxidation of Cu(110) and water adsorption on CuO_x at near ambient conditions

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The oxidation of the Cu(110) surface has been studied by in situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS) at ambient oxygen pressures and high temperatures. Different CuO_x species have been identified unambiguously. The different adsorption behaviors of H_2O on these CuO_x surfaces have been investigated in situ systematically at near ambient conditions.

COLL 484

New mechanism of atomic manipulation: Bond-selective molecular dissociation via thermally activated electron attachment

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We report a new mechanism of (bond-selective) atomic manipulation in the scanning tunneling microscope (STM). We demonstrate a channel for one-electron induced C-Cl bond dissociation in chlorobenzene molecules chemisorbed on the Si(111)-7x7 surface, at room temperature and above, which is thermally activated. We find an Arrhenius thermal energy barrier to one-electron dissociation of 0.8 ± 0.2 eV, which we correlate explicitly with the barrier between chemisorbed and physisorbed precursor states of the molecule. Thermal excitation promotes the target molecule from a state where one-electron dissociation is suppressed to a transient state where efficient one-electron dissociation, analogous to the gas phase negative ion resonance process, occurs. We expect the mechanism will apply in many surface systems, and not just in STM manipulation, but in photon and electron beam stimulated (selective) chemistry.

COLL 485

Nanoparticle heating: Basic science and biological applications

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Recently a concept of nanoparticle heating localized to nano/micro scale regions have been promoted as cell-level selective hypothermia of cancer. However, an analysis of the diffusive heat flow equation shows that heating powers generated by rf magnetic fields and continuous lasers do not lead to a meaningful heating at nanoscale. Biologically relevant temperature increase can be achieved with a large number of nanoparticle heat sources, however, over macroscopic regions. A realistic approach for producing a significant local temperature rise on nanometer length scales is heating by high-power pulsed lasers. In this context, we demonstrated, consistently with the experiment, that such heating may melt or even “evaporate” nanoparcles into the solution without formation of macroscopic vapor. The vapor formation suppression is explained by the curvature-induced Laplace pressure close to the nanoparticle, which inhibits boiling. We observe similar behavior for water and organic fluids, underscoring generality of the results.

COLL 486

Gas-to-particle nucleation in multicomponent systems: Nucleation mechanisms and cluster properties

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The underlying assumptions of classical nucleation theory severely hamper its predictive capabilities for nucleation in multi-component systems. Aggregation-volume-bias Monte Carlo simulations are applied (i) to predict gas-to-particle nucleation free energy landscapes and gain a molecular-level understanding of nucleation pathways and (ii) to probe the properties of pre-critical clusters and critical nuclei for mixtures containing water, alcohols, and alkanes. First principles molecular dynamics simulations are used to investigate speciation in nanodroplets containing water, acids, and bases.

COLL 487

Modeling of self-standing nanoparticle membranes, containers, tubes, and superlattices

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First, we discuss our coarse-grained molecular dynamics simulations of the recently prepared self-standing NP-membranes, formed by gold nanoparticles (NP) capped with alkanethiol ligands. These simulations reveal that the structure, stability, and mechanical properties of the NP-membranes are controlled by the ratio of ligand length and particle core radius. We show that NP-containers can potentially be also formed and used for molecular storage, delivery, and chemical reactions. Next, we describe our modeling of self-assembled NP-superlattices by considering bulk van der Waals and dipole-dipole interparticle interactions. We study the packing principles of ligated platinum nanocubes, which were experimentally found to assemble into simple cubic or fcc structures. Our modeling reveals a novel packing principle, explaining the formation of fcc structures for truncated nanocubes. We also model spherical particles with dipole-dipole coupling and demonstrate that they can form a rich spectrum of structures with different packing.

COLL 488

Effect of carbon nanospheres on membrane stability

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We investigated the translocation of carbon nanopsheres of different sizes through lipid bilayers. Various fullerenes serve as model system for carbon nanospheres. Using all-atom (AA) and coarse-grained (CG) Molecular Dynamics (MD) simulations, we calculated the change in free energy when C60, C180, and C540 fullerenes are transferred from water to the interior of a dioleoylphosphatidylcholine (DOPC) bilayer. Upon entering the lipid bilayer, the larger fullerene (2.4 nm in diameter) causes local distortions in the bilayer surface which were previously observed in carbon nanotube simulations. These local distortions, however, do not lead to any free energy barriers. From the free energy profiles, we deduce spontaneous absorption of all three fullerene types. Qualitative agreement was observed when comparing fullerene partitioning in water/bilayer systems to water/hexane systems. In contrast to these nonspecific single fullerene properties, extensive CG-MD simulations of fullerene rich lipid bilayers reveal substantial fullerene-size effects on the bilayer stability. While CG-MD simulations indicate that bilayer bound C60 aggregates have little effect on the bilayer structure, C540 aggregation has extreme effects. This destabilization phenomenon likely has implications for understanding the cytotoxic mechanisms of carbon nanoparticles upon uptake by biological cells.

COLL 489

Emergent collective behavior of autonomous nano/microparticles

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One of the more interesting recent discoveries has been the ability to design nano/microparticles which catalytically harness the chemical energy in their environment to move autonomously. These "bots" can be directed by chemical and light gradients. Further, our group has developed systems in which chemical secretions from the translating micro/nanomotors initiate long-range, collective interactions among the particles via self-diffusiophoresis. This behavior is reminiscent of quorum sensing organisms that swarm in response to a minimum threshold concentration of a signaling chemical. We will discuss recent experimental results, as well as approaches to the modeling of the complex emergent behavior of these particles.

COLL 490

Surfactants and nanoparticless at oil/water interfaces

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The physical properties of many oil/water systems depend on their surface energies. Through orthogonal pathways, surfactants and nanoparticles are each able to concentrate at and stabilize oil/water interfaces. Although the behavior of surfactants and nanoparticles at interfaces have been separately established, the behavior of systems with both components in coexistence requires further investigation. Here we show that molecular dynamics computer simulations can be used as a valuable tool in investigating the behavior of systems containing both nanoparticles and surfactants at oil/water interfaces. In these simulations we find a rich interconnection between the behavior of surfactants and nanoparticles, including both synergy in lowering the oil/water interfacial tension and competitive adsorption. Furthermore, simulations where the surfactants are bound onto the nanoparticle surface show that even moderate coverage of the nanoparticles by surfactants disrupts the nanoparticle aggregation behavior.

COLL 491

Asymmetry of coated spherical nanoparticles in solution and at liquid/vapor interfaces

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Nanoparticles in solution are often stabilized with functional coatings to prevent aggregation. I will present recent simulation results showing that small spherical nanoparticles produce highly asymmetric coating arrangements, when coated with simple polymer chains. These coatings are not symmetric even when extremely uniform grafting arrangements and full coverages are employed. Also, I will discuss the geometric properties which dictate the coating shape. When particles are placed in an anisotropic environment, such as the liquid/vapor interface, the asymmetric coatings are amplified and oriented by the surface. Particle shape and its responsive behavior is seen to strongly influence interactions. Implications and examples of controlled self-assembly will be presented.

COLL 492

Redox surface reactions of ferric oxide nanoparticles and particle aggregates with flavins

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Ferric oxides are important mineral components of soils and subsurface environments that commonly exist as nanophases. Under anoxic conditions, dissimilatory iron-reducing bacteria utilize ferric oxides as terminal electron acceptors for respiration. Recently, flavins, including flavin mononucleotide (FMN) and riboflavin, were found to be released by *S. oneidensis* MR-1 to the growth medium, and these redox-active flavin compounds are suspected to shuttle electrons between the bacterial cells and ferric oxides. In this work, the kinetics of electron transfer between ferrihydrite, lepidocrocite, or goethite and fully reduced flavins was studied using either stirred batch reactors or a stopped-flow apparatus in the pH range 5-8 in anaerobic chamber. The hydroquinone form of flavins rapidly reduces and dissolves ferrihydrite and lepidocrocite in minutes, generating stoichiometric amounts of Fe(II) and oxidized flavins. The rate was slower for poorly crystalline ferrihydrite than for crystalline lepidocrocite. The reduction of goethite, in contrast, required hours of contact. The reduction rate of goethite decreased as the pH increased.

COLL 493

Simulated atmospheric processing of iron oxyhydroxide minerals at low pH: Roles of particle size, light and oxyanion in iron dissolution

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Over the last several decades, it has been recognized that 30 % of the world ocean is roughly comprised with high nutrient low chlorophyll regions where the phytoplankton primary productivity is limited by the bio-available iron concentration. A number of recent studies have shown that iron dissolution in Fe-containing dust aerosol can be linked to source material, mineralogy, and iron speciation. In this research work, we combine dissolution measurements along with spectroscopy and microscopy to focus on nanoscale size effects in the dissolution of Fe-containing minerals in low-pH environments and the importance of acid type, including HNO_3, H_2SO_4, and HCl, on dissolution. Furthermore, the effect of oxyanions, PO_4^{3-} and CO_3^{2-}, on iron dissolution will be discussed. These measurements are done under light and dark conditions so as to simulate and

distinguish between daytime and nighttime atmospheric chemical processing. Both size, nano- versus micron-sized particles, and oxyanion are found to play significant roles in the dissolution of α-FeOOH under both light and dark conditions. The current study highlights these important, yet unconsidered, factors in the atmospheric processing of iron-containing mineral dust aerosol.

COLL 494

Size-dependent dissolution of hematite nanoparticles: Implications for iron cycling in surface waters

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In natural systems, the redox cycling between ferrous and ferric iron influences iron bioavailability and has implications for pollutant fate. In this study, two sizes (approximately 10 and 40 nm) of hematite (α-Fe_2O_3) nanoparticles were synthesized to determine the role of particle size in interfacial processes relevant to iron dissolution and redox cycling. These include reductive dissolution with ascorbic acid, proton-promoted dissolution at low pH, ligand-promoted dissolution with oxalate, and photoreductive dissolution in irradiated suspensions with various forms of dissolved organic matter, all of which were investigated over a range of pH values. Generally, for all dissolution processes, rates of soluble iron production from 10 nm particles far exceeded that of the 40 nm particles, even after accounting for the measured difference in primary particle specific surface area determined via BET and the aggregation state of the suspension determined by light scattering. Thus, we attribute these results to unique surface chemical properties associated with smaller primary particle sizes of hematite. Ongoing work is exploring the implications of these results for iron-mediated (photo)chemical processes in surface water.

COLL 495

Redox driven atom exchange in Fe oxides

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Iron oxides are ubiquitous. Essentially anywhere that iron is exposed to oxygen, iron oxides form. These tiny, often nanoscale, particles are responsible for most

of the red, yellow, green, and black color you observe around you and they profoundly influence the quality of our water, air, and soil through the biologically-driven redox cycling between ferric (Fe^{III}) and ferrous iron (Fe^{II}). We have used stable Fe isotopes in conjunction with ^{57}Fe Mössbauer spectroscopy to study redox reactions between ferrous Fe and Fe oxides. Our results, as well as others have shown that sorbed Fe(II) is oxidized by Fe(III) in Fe oxides, such as goethite, hematite, ferrihydrite, and magnetite and that Fe(II)-Fe(III) electron transfer initiates extensive atom exchange between the Fe oxide and aqueous Fe(II). Here we explore whether redox driven atom exchange will occur under more complex biogeochemical conditions by measuring the extent of atom exchange using stable Fe isotopes. More specifically, we are investigating how important biogeochemical processes, such as cation substitution, anion sorption and microbial respiration influence the rate and extent of atom exchange. Our goal is to determine if redox driven atom exchange is likely to occur in natural environments.

COLL 496

Impact of aggregation state on the evolving reactivity of iron oxide nanoparticles

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Mineral surfaces play important roles in the reductive degradation of organic contaminants in natural and engineered environmental systems. Here, we present results of a suite of experiments in which the rates of organic contaminant degradation are quantified and solid materials are characterized , before, during, and after reaction. In general, reactivity is quite dynamic, often showing dramatic increases or decreases with repeated and/or continued reaction. Increases in aggregation typically result in decreased rates of degradation whereas precipitation of magnetite typically results in increased rates of reductive degradation. By pairing careful solid-state characterization with quantitation of rates of degradation, we link changes in mineralogy and accessible surface area of natural and synthetic materials caused by the reductive transformations of selected contaminants with the evolving kinetics of contaminant degradation.

COLL 497

Potential effects of nanotitania in benthic systems

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Nanotechnology is rapidly moving from discovery to commercialization. This revolution in atomic and molecular engineering promises many environmental and human health benefits such as dramatic improvements in efficiency, reduced resource use and waste, and astounding improvements in medical diagnostics and therapeutics. Yet, the risks posed by nanotechnology to ecological and environmental health have not been rigorously assessed, and without these data a meaningful regulatory framework to protect human and environmental health and safety and guide the development of nanomaterials cannot be formulated. While the defining characteristic of nanomaterials is their size, subtle changes in size, shape and surface functionality have profound effects on chemical and physical behavior. This presentation will provide a detailed overview of the catalytic activity of nanotitania and relate these physical and chemical characteristics to explain the range of seemingly conflicting reports about its nanotoxicity in environmental systems, with special attention to the benthos of aquatic systems.

COLL 498

Development of a high-throughput dual fluorescence viability assay for algae

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Interactions of metallic nanoparticles (NPs) with freshwater microalgae, *Chlamydomonas reinhardtii*, were evaluated to understand the fate and toxicity of NPs in the environment. Algal cultures were exposed to nanoscale, zerovalent metals Ag, Cu, Fe, Zn, and core-shell structures CuAg and CdSe. Equivalent concentrations of metal salts were also tested. Our results indicate that all tested NPs were toxic; with IC_{50} values ranging from 0.004 mg/L to 4 mg/L. NP toxicity was closely related to dissolved metal concentrations. Algal responses to NP exposure during exponential phase were statistically similar to those in stationary phase. Since current methods for assaying the growth and viability counts of algae are slow and labor-intensive, a dual fluorescence assay was developed for rapidly screening samples varying in NP characteristics, water chemistries, and algal metabolisms. The results from the two methods were in agreement,

indicating that the assay would be valuable in high-throughput analyses of dose-response as well as toxicity mechanisms.

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Statistical evaluation of DLS photon count rate as a surrogate measurement for nanoscale particles count in three southern California wastewaters

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Techniques to monitor biogenic and manufactured nanoscale particles in wastewater are still evolving. Instruments that use Dynamic Light Scattering (DLS) techniques are currently used to measure nanoscale particles size distribution in aqueous samples. However, instruments to measure nanoscale particles count are not readily available. This study evaluated the use of photon count rate (kilo counts per second (kCPS)) during DLS measurement (Malvern-ZS) as a surrogate measure for nanoscale particles count in wastewater samples from three treatment plants. A Method Validation study using five dilutions, 12 replicates, multiple days and multiple analysts was performed to evaluate detection limit, accuracy and precision of such analyses. Results indicated that photon count rate can be a viable surrogate measure ($R^2 > 0.95$, Std. Dev < 10%) for nanoscale particles count in wastewater samples. Spike analyses using nanosilica yielded more than 98% recovery. The presentation will include detailed discussion of the Methods Validation Study.

COLL 500

Detection and formation kinetics of nanosized Pb(IV) corrosion product in drinking water

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PbO_2 nanoparticle is a new form of Pb(IV) corrosion product discovered in the drinking water distribution system. It is formed via the chlorination of lead-containing plumbing materials and has been found important in controlling lead contamination in drinking water. The identification and quantification of PbO_2 nanoparticle in water samples using ICP-MS, however, is difficult due to its

extremely low solubility during acid digestion. In this study, an iodometric method that is able to quickly detect PbO_2 spectrometrically was developed. Spiked experiments showed that this method can detect 0.02 to 20 mg/L PbO_2 in 10 min with recoveries greater than 90%. The formation kinetics of PbO_2 nanoparticle from the chlorination of Pb(II) solids in typical drinking water was also explored.

COLL 501

Mechanistic diversity in membrane binding by C2A domains of synaptotagmin isoforms

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Synaptotagmin (Syt) triggers Ca^{2+}-dependent vesicle fusion via tandem C2 domains, termed C2A and C2B. Different isoforms are active in different cell types, including neurons (SytI) and pancreatic β cells (SytVII). Here, docking of SytIC2A and SytVIIC2A to physiological membrane lipid mixtures is quantitatively compared using stopped-flow and steady-state fluorescence. In agreement with previous studies, the Ca^{2+} sensitivity of membrane binding is ~8-fold higher for SytVIIC2A. Association and dissociation rate constants for SytVIIC2A were found to be respectively ~3-fold and ~200-fold slower than SytIC2A, seemingly reflecting its function in the slower process of insulin secretion. The dependence of these parameters on phosphatidylinositol-4,5-bisphosphate (PIP_2), a target lipid for some C2 domains, was minimal. Preliminary results indicate that SytVIIC2A docks to membranes via hydrophobic and electrostatic interactions, while the membrane docking interaction of SytIC2A is predominantly electrostatic. Thus, these homologous domains exhibit distinct mechanisms of membrane binding that may reflect differences in function.

COLL 502

Assembly of large unilamellar vesicles at the aqueous/aqueous interface

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The partitioning behavior of fluorescently-labeled large unilamellar vesicles (~200 nm) in a polyethylene glycol (PEG):dextran aqueous two-phase system (ATPS)

is observed. Changes in bilayer PEGylation are shown to impact partitioning such that vesicles without PEGylated lipids partitioned between the interface and the dextran-rich phase; while PEGylated vesicles in the brush regime partitioned exclusively to the interface. Increasing concentration of PEGylated vesicles led to an increase in interfacial area. Occurrence of fusion between vesicles at the ATPS interface was evaluated by fluorescence recovery after photobleaching.

COLL 503

Mechano-stimulation of fibroblasts by adjusting viscous drag of mobile cell linkers in biomembrane-mimicking substrates

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Previous studies of fibroblasts on substrates of tunable elasticity with immobilized cell linkers have shown that changes in substrate viscoelasticity may have a crucial affect on cell adhesion and morphology and other pivotal cellular processes. Here we report a series of complimentary experiments utilizing biomembrane-mimicking cell substrates based on polymer-tethered lipid multi-bilayer, in which laterally mobile cell linkers enable the free assembly and disassembly of focal adhesions and the viscous drag of cell linkers can be regulated by the number of bilayers in a multi-lipid bilayer stack. To explore the underlying mechanisms of mechano-regulation on these viscous substrates, the cellular response (morphology, shape fluctuations, migration and cytoskeleton organization) is analyzed on substrates with different cell linkers like E-Cadherin or Laminin. Furthermore, force traction microscopy results are presented, which reveal low cellular traction forces on multi-bilayer systems, thus confirming the lubricating affect of the biomembrane-mimicking substrate.

COLL 504

Crystallization induced by electrostatic correlations in vesicles of mixed-valence ionic amphiphiles

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Charged amphiphilic molecules, including molecules with biological motifs, have been predicted to organize into elastic membrane or crystalline shells with non-spherical shapes. We demonstrate that pure electrostatic interaction allow (-1) anionic water insoluble amphiphiles and (+3) cationic amphiphiles, which form only micelles in water, to co-assemble into buckled vesicles. The strong interaction between the +3 and -1 head groups increases the cohesive energy of the amphiphiles and favors the formation of crystallized membranes or shells that facet spontaneously into buckled shapes predicted by simulations of vesicles with heterogeneous elastic properties. In situ small-angle and wide-angle X-ray scattering (SAXS-WAXS) experiments conducted at the Advanced Photon Source DND-CAT confirm the presence of crystalline bilayers. Our simulations verify that ionic lateral correlations among the oppositely charged head groups of the co-assembled amphiphiles are responsible for the observed tail crystallization.

COLL 505

DNA-inks for 3D printing: DNA composites for the rapid prototyping of scaffold in bioengineering applications

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3-D printing, which is also called rapid-prototyping, has become a fantastic technique that allows for the manufacture of precise three-dimensional objects with intricate complexity. Rapid-prototyping instruments work by directing a UV-laser into a solution containing soluble photoactive monomers, which polymerize at the exposure of the laser beam. A variety of tissues are being engineered using this approach including fabricated artery, bladder, and skin. Since DNA is a powerful and versatile biopolymer, which has self-assembly properties, it may serve important roles in 3-D printing technologies. The synthesis of photoactive styrene derivatives designed to bind DNA and polymerize under UV light will be described. for the first time, the characteristics of the rapid- prototyping of bioengineering scaffolds and its applications will be explored.

COLL 506

Bilayer-modifying potential of limonene and its metabolites

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Membrane protein function depends on lipid bilayer properties, which may account for some of the undesired clinical effects of amphiphatic drugs that modify bilayer properties. In this study, we assessed whether D-limonene and its metabolites (perillyl alcohol, perillaldehyde, and perillic acid) alter lipid bilayer properties, as sensed by bilayer-spanning gramicidin (gA) channels, using a fluorescence assay and single-channel electrophysiology. D-limonene and its metabolites are terpenes that are found in a variety of foods. They have been shown as potential cancer prevention and treatment agents. Using the fluorescence assay, we find that at micromolar (nominal) concentrations: D-limonene decreases gA channel activity, perillyl alcohol and perillaldehyde increase activity, and perillic acid has no apparent effect. When examined using single-channel electrophysiology, each terpene increased gA channel lifetime and appearancerate. The changes in gA channel function were observed at low membrane concentrations (mole fraction ~0.02-0.03), indicating that these terpenes are potent bilayer modifiers.

COLL 507

Tethered lipid bilayer membranes assembly on gold by fusion of functionalized lipid vesicles

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Lipid vesicles with functional chemical groups were designed to promote vesicle fusion on atomically flat template stripped gold (TSG) surface which is favorable for low defect density molecular assembly. Vesicles composed of 2.5 mol% 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N*-poly(ethylene glycol)-2000-*N*-[3-(2--(pyridyldithio)propionate)] (DSPE-PEG-PDP) / 97.5 mol% POPC fused and formed tether lipid bilayer membranes (tLBMs) on TSG surfaces as determined by atomic force microscopy (AFM) topography and force spectroscopy measurements acquired under physiological conditions. The DSPE-PEG-PDP molecule containing a disulfide group is incorporated for Au-thiolate bond formation, which increases vesicle-substrate interactions and promotes vesicle fusion on TSG. As a control, vesicles composed of 100 mol% POPC did not interact with unfunctionalized hydrophobic TSG surface and only adsorbed on oxygen plasma treated hydrophilic TSG. Besides, vesicles composed of 2.5 mol% 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[methoxy (poly-ethylene glycol)-2000] (DSPE-PEG) / 97.5 mol% POPC showed no indication of membrane formation on TSG, suggesting that the disulfide group in DSPE-PEG-PDP is critical for promoting vesicle fusion and membrane formation on Au.

Analysis of force-distance curves for 2.5% DSPE-PEG-PDP / 97.5% POPC tLBMs on TSG yielded a breakthrough distance of 4.8 ± 0.4 nm, which is about 1.7 nm thicker than that of POPC LBM formed on mica. Thus the PEG group serves as a spacer layer between the tLBM and TSG surface. Fluorescence microscopy results indicate these tLBMs also have greater mechanical stability than un-tethered LBMs made from the same vesicles on mica. Although AFM images showed incomplete tLBMs on TSG surfaces, complete surface coverage can be achieved by annealing samples in aqueous solution or during AFM scanning after exposure to functionalized vesicles. These large-scale manufacturing compatible methods introduced in this study are promising for fabricating individually electrically addressable tLBM arrays designed for high-throughput electrochemical measurements of protein-membrane interactions.

COLL 508

Convective and field-directed assembly of titania nanoparticle thin films

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Titanium dioxide nanoparticles are important components of existing and emerging energy-harvesting strategies, including their use in dye-sensitized solar cells and other photocatalytic and photovoltaic devices and materials. In this talk, I will present recent techniques we have developed in which suspensions of anisotropic titania nanoparticles are used to create thin films with novel optical, mechanical and thermal transport properties. Using both convective and field-directed convective assembly, we are able to tailor the thin film structure, including particle orientational order and thickness. In convective assembly using a fixed-blade flow coating apparatus, the blade angle, particle concentration and blade speed are used to control particle orientational order and film thickness. Directing convective assembly with ac electric fields provides an additional form of control in terms of the particle orientational coupling to the external field, as well as field-induced polarization interactions between particles. This suggests new means of tailoring assembly by "programming" particles to respond to external fields through shape or surface chemistry, which will enable new structures and properties of these versatile materials.

COLL 509

Patchy particle fabrication and self-assembly

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Anisotropic colloidal particle assemblies have great potential in photonics. However, the synthesis and functionalization of anisotropic particles remains a challenge. We will present a method to fabricate patchy particles in which carboxylic acid containing colloidal clusters are encapsulated by inert shells in a two-step swelling and polymerization process. The resulting patchy particles can then be functionalized further with alcohol containing small molecules or block copolymers using standard ester formation protocols. Finally, patchy particles that have been functionalized with palladium SCS pincer complexes and pyridine derivatives can be self-assembled into larger architectures using metal coordination providing a proof of principle for a self-assembly strategy towards anisotropic colloidal particle assemblies.

COLL 510

DNA architechtures for templated material growth

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We will present a methodology that allows for the coupling of biology and electronic materials, where double stranded DNA serves as a template for electronic material growth. Self-assembled DNA structures allow for a variety of patterns to be achieved on the nanometer size scale that are difficult to achieve using conventional patterning techniques. Herein, we describe the procedures for the creation of self-assembled DNA nanostructures in aqueous and non-aqueous media, and their subsequent deposition onto substrates of interest. DNA self assembly under non-aqueous conditions has yet to be presented in literature, and is necessary if unwanted oxidation of certain electronic substrates is to be avoided. Solubilization of the DNA in non-aqueous solvents is achieved by replacing charge stabilizing salts with surfactants. Retention of DNA hierarchical structure under both conditions will be presented by observing the structures using AFM imaging, gel electrophoresis, and circular dichroism spectroscopic studies.

COLL 511

Gold nanoparticles from thermo-responsive bottle brush block copolymers

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@font-face { font-family: "宋体"; }p.MsoNormal, li.MsoNormal, div.MsoNormal { margin: 0in 0in 0.0001pt; text-align: justify; font-size: 8pt; font-family: "Times New Roman"; }p.PreprintBody, li.PreprintBody, div.PreprintBody { margin: 0in 0in 0.0001pt; text-align: justify; text-indent: 0.25in; font-size: 8pt; font-family: "Times New Roman"; }div.Section1 { page: Section1; } Gold nanoparticles have been extensively investigated due to their characteristic size- and shape-dependent optical, magnetic, and electronic properties and thus their potential applications including photon conversion, catalysis. Therefore the synthesis and characterization of gold nanoparticles with controlled morphology, size have been the focus of increasing research interest.   In this contribution, we use a thermo-responsive block copolymers (PDMA-P(PEGMA)) to stabilize gold nanostructures formation without any additional reduction agent. For example, when 1.0 wt% of $PDMA_{40}$-$P(PEGMA)_{11}$ block copolymer aqueous solution was mixed with of 1.0 mM $HAuCl_4$ solution, the solution gradually turned pink after stirring for 24h and at 20 ^oC, indicating the formation of ultrafine gold nanoparticles. TEM showed that gold nanoparticles with a relatively uniform size were formed (Figure 1A). UV visible absorption shows a maximum adsorption (surface plasmon absorption) at 525 nm (Figure 1B).

COLL 512

Peptide-mediated synthesis of Pd nanocrystals

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Here we report a peptide-mediated synthesis of Pd NCs in aqueous solution with controllable size in the sub-10 nanometer regime. The specific multifunctional peptide Q7 selected using Phage-Display technique can bind to the Pd NC surface and act as a stabilizer to mediate Pd crystal nucleation and growth. At the nucleation stage, Q7 bound to and helped stabilize the different-sized small Pd NC nuclei achieved using different concentrations of the external reducing agent, $NaBH_4$. At the growth stage, Q7 played the dual role of binding to and reducing the precursor onto the existing nuclei, which led to the further controllable growth of the Pd NCs. By using the variable sizes of nuclei as seeds, and by introducing different amounts of precursors Pd NCs with tunable sizes from 2.6-6.6 nm were achieved with good size distribution. Morphology control of Pd NCs may also be discussed.

COLL 513

Universal surfactant for water, oils, and CO_2

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A trichain anionic surfactant sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulfonate (TC14) is shown to aggregate in three different types of solvent: water, heptane and liquid CO_2. Small-angle neutron scattering (SANS) has been used to characterize the surfactant aggregates in water, heptane and dense CO_2. Surface tension measurements, and analyses, show that addition of a third branched chain to the surfactant structural template is critical for sufficiently lowering surface energy, tipping the balance between a CO_2 incompatible surfactant (AOT) and CO_2-philic compounds that will aggregate to form micelles in dense CO_2 (TC14). These results highlight TC14 as one of the most adaptable and useful surfactants discovered to date, being compatible with a wide range of solvent types spanning the high dielectric polar solvent water, through to alkanes with low dielectrics, and even being active in the uncooperative and challenging solvent environment of liquid CO_2.

COLL 514

Poly(amino acid)s-mediated synthesis of spatially organized Pt nanoparticles

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Nanometer-sized noble metal particles are being increasingly studied for use in various applications including photochemistry, electrochemistry, optics, and catalysis. Recently, extensive efforts have been made to improve nanoparticle dispersion to enhance its performance using various surfactants, dendrimers and polyelectrolytes which can tune colloidal interactions. However, it is still challenging to establish a technology in which spatial organization of metal nanoparticles is finely controlled at varied length scales. Here we present that in situ sol-gel polymerization of metal precursors incorporated into self-assembling poly(amino acid) nanostructure would generate metal nanoparticles with regular spacing at the nanometer scale. This hypothesis was examined using poly(amino acid)s substituted with alkyl chains to form various morphologies from a spherical micelle to a bilayer structure. Platinum precursors (K_2PtCl_4) were mixed with alkyl-substituted poly(amino acid)s solution followed by reduction to activate sol-gel polymerization to form Pt particles. Specifically, alkyl-substituted poly(amino acid)s with DS of 5 % were assembled into a vesicle with an average diameter of 100 nm, and also presented Pt nanoparticles with diameter of 2 to 5 nm exclusively within a bilayer of the vesicle. Furthermore, the resulting Pt nanoparticles showed a significantly enhanced electro-catalytic activity as compared with Pt particles polymerized via bulk sol-gel polymerization. Taken together, the results of this study demonstrated that the size and spacing of metallic particle can be controlled using a self-assembling polymeric template. The resulting particles present strong potentials to significantly improve performance of a variety of energy storage and generation systems.

COLL 515

Open air and simple method to synthesize narrowly distributed and size tunable PbSe nanocrystals

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An open air and simple method to synthesize narrowly distributed and size tunable PbSe nanocrystals is reported here. Oleylamine was used as either capping agent or solvent. $PbCl_2$ complexed with oleylamine was used as the lead precursor. Se powders dissolved in oleylamine were used as the Se precursor. The size and shape of the PbSe nanocrystals were tuned by changing injection temperature and reaction temperature to obtain the best synthetic conditions. The sizes of the PbSe nanocrystals ranged from 7.9 nm to 13.9 nm. The shapes of the PbSe nanocrystals were either spherical or cubic. The as-synthesized

colloidal PbSe nanocrystals were characterized by transmission electron microscopy.

COLL 516

Novel porous materials derived from colloidal bijels

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Porous materials with well-defined microstructure are valuable in energy applications including catalysis, fuel cells, and photovoltaics, among others. At the length scales relative to these applications, direct manipulation to achieve a desired microstructure would be difficult and expensive, and alternative means for tuning the material's microstructure are needed. Here, we present a new route for the synthesis of ceramic, metallic, and inorganic porous materials with tunable bicontinuous morphology using a bicontinuous interfacially jammed emulsion gel (bijel) template. Selective polymerization of a continuous fluid phase results in a macroporous polymer with a 3D spinodal architecture, which serves as a template for the microstructures reported here. The polymer crosslinking density is exploited to provide for different modes of materials processing including nanocasting, nanoparticle infiltration, and structural inversion, producing a novel family of porous structures and composites including materials with hierarchical bicontinuous pore morphology. The potential relevance of these materials in energy applications will be discussed.

COLL 517

Electronic structure as a predictor of hydrated oxide surface reactivity

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It is now well-established that oxide surface structure is dependent on the conditions to which the surface is exposed, and that clean surface structures found in ultra-high vacuum conditions can evolve significantly as a function of water and oxygen exposure. However, the structure-property relationships of hydrated oxides remain poorly understood, limiting both the ability to interpret empirical trends in environmental interface reactivity and the rational design of hydrated surfaces with tailored reactivity. The oxide-water interface introduces complexity not found in analogous ultra-high vacuum surface science, complicating the goal to identify the key factors driving reactivity. When coupled with an ab initio thermodynamic framework, density functional theory can be used to study and predict structure and important classes of reactivity at hydrated

oxide surfaces. Examples are presented in which electronic structure analysis is used to provide new molecular-level understanding of adsorption processes at oxide-water interfaces. The focus is on the uptake of heavy metal cations to form inner-sphere surface complexes, with implications and preliminary results for broader classes of reactivity.

COLL 518

Structure and reactivity of oxide surfaces as revealed through a chemical bonding analysis

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Chemical bonding has often been ignored in favor of physics based energetic considerations in attempts to understand the structure and stability of oxide surfaces. Recent results indicate that chemical bonding plays a major role in determining what surface structures will form. Various $SrTiO_3$, MgO, and NiO surface structures are examined from a chemical bonding perspective. A bond valence analysis of these oxide surfaces closely matches the physics based energy calculations. Further, the bond valence analysis reveals not only the overall stability of the surface, but which surface atoms are under- or over-coordinated, and therefore which are likely to bind foreign species.

COLL 519

Formation of gold(I) edge oxide at flat gold nanoclusters on an ultrathin MgO film under ambient conditions

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Density functional theory calculations were applied to study the adsorption and dissociation of molecular oxygen on a Au_{14} cluster supported on the 2 ML thick MgO film over the Ag(111) surface. The O_2 molecule adsorbs exothermically at the cluster support interface. With increasing oxygen coverage the adsorption becomes weaker but the cluster can accommodate upto 10 O_2 molecules. Upon adsorption oxygen is clearly activated which is seen as an elongated O-O bond length and changed magnetic moment. The calculations show clear

thermodynamic driving force towards dissociation, which is also kinetically accessible with the activation barrier of 0.5 eV. The charge analysis shows that Au is cationic or neutral. The thermodynamic data is compiled to the plot of Gibb's free energy of adsorption using atomistic thermodynamics.Among the calculated structures the most stable structure at ambient conditions is the one which shows one dimensional edge oxide at the perimeter of the Au cluster. Reference: P. Frondelius et al. Angew. Chem. Int.49, 7913 (2010)

COLL 520

WITHDRAWN

COLL 521

Vapor deposition of azide and methyl-terminated siloxane monolayers onto silicon oxide and the role of hydrolysis

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A convenient, laboratory scale method for the vapor deposition of siloxane monolayers onto silicon oxide surfaces at elevated temperature and under reduced pressure was developed. The deliberate addition of water as a reactant was necessary to form complete monolayers and was accomplished through the *in situ* dehydration of $MgSO_4{\cdot}7H_2O$. The synthesis and deposition of tri(deuteromethoxy)silanes allowed the clear monitoring of methoxy group hydrolysis using Fourier-transform infrared (FTIR) spectroscopy. Complete monolayers were formed when sufficient water was present to hydrolyze all methoxy groups. The conditions developed for the vapor deposition of complete, hydrolyzed monolayers were applied to the deposition of pure and mixed azide-terminated monolayers. Next, click chemistry was used to covalently attach ethynyl-terminated molecules to the azide-terminated surfaces. In addition to FTIR spectroscopy, the monolayers were characterized using x-ray photoelectron spectroscopy (XPS), ellipsometry, and water contact angle goniometry.

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Using second harmonic generation to understand specific ion effects at the silica/ and modified-silica/water interface

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The ability of ions to interact with biological and environmental interfaces depends not only on their charge but also their polarizability. Indeed, Hofmeister discovered in the late 19th century that different ions of similar charge could have different effects on protein stability. Studies of specific ion behavior at interfaces have seen a recent revival. To observe subtle changes associated with these specific ion effects, surface specific techniques are often required. The surface specific technique second harmonic generation (SHG) is an ideal technique for such studies because it can report on the change in surface charge density at an interface in real time. Here we demonstrate how SHG can be used to track specific ion effects for silica and other acidic and basic surfaces as a function of pH. Determining how different ions influence interfacial behavior is key to understanding acid-base chemistry and binding events at interfaces.

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Chemical vapor deposition of three aminosilanes on silicon dioxide: Surface characterization, stability, effects of silane concentration, and cyanine dye adsorption

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Covalently bonded monolayers of two monofunctional aminosilanes (3-aminopropyldimethylethoxysilane, APDMES, and 3-aminopropyldiisopropylethoxysilane, APDIPES) and one trifunctional aminosilane (3-aminopropyltriethoxysilane, APTES) have been deposited on dehydrated silicon substrates by chemical vapor deposition (CVD) at 150 °C and low pressure (a few Torr) using reproducible equipment. Standard surface analytical techniques such as x-ray photoelectron spectroscopy (XPS), contact angle goniometry, spectroscopic ellipsometry, and atomic force microscopy, have been employed to characterize the resulting films. These methods indicate that essentially constant surface coverages are obtained over a wide range of gas phase concentrations of the aminosilanes. XPS data further indicate that the N1s/Si2p ratio is higher after CVD with the trifunctional silane (APTES) compared to the monofunctional ones, with a higher N1s/Si2p ratio for APDMES compared to that for APDIPES. AFM images show an average surface roughness of 0.12-0.15 nm among all three aminosilane films. Stability tests indicate that APDIPES films retain most of their integrity at pH 10 for several hours and are more stable than APTES or APDMES layers. The films also showed good stability against storage in the laboratory. Optical absorption measurements on adsorbed cyanine dye at the surface of the aminosilane films show the formation of dimer aggregates on the surface. This is further supported by ellipsometry measurements. The concentration of dye on each surface appears to be consistent with the density of the amines.

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Solution ^{1}H NMR investigation of functionalized silicalite nanoparticles

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Porous nanomaterials, such as zeolites, have very large surface area that can be used to control their chemical, biological and catalytic activities. Through functionalization, the properties of the nanocrystalline zeolite external surface can be tailored for specific applications. Characterization of organic molecules deposited on a substrate is a key to the successful chemical modification of nanomaterial surfaces. In this investigation, proton solution NMR technique was used to characterize qualitatively and quantitatively surface bound functional groups. The feasibility of using ^{1}H solution NMR for full structural elucidation of small organic guests covalently attached to nanoparticles was demonstrated. It has also been shown that ^{1}H solution NMR is surface selective and can provides direct spectroscopic evidence of the supramolecular binding of APDMMS to the external surface of nanocrystaline silicalite.

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Self-assembly of complex crystals and quasicrystals from patchy and polymer-tethered nanoparticle shape amphiphiles

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Using short, organic polymer “tethers” to organize nanoparticles is a promising route to bottom-up self-assembly of complex nanostructured materials [1]. We present simulation predictions of self-assembled structures that result from patchy nanoparticles functionalized with a countable number of short “tethers”. These novel shape amphiphile building blocks exhibit complex ordering patterns reminiscent of liquid crystals, surfactants and block copolymers but with additional local and mesoscale structure arising from the combination of amphiphilicity and particle packing. We show how various measures of tethered

nanoparticle anisotropy, including building block shape and the number and location of tethers, as well as volume fraction and solvent selectivity, can be combined and exploited to achieve complex structures, including quasicrystals [2] and analogs of ionic atomic and colloidal crystals [3,4]. [1] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, "*Tethered nano building blocks: Towards a conceptual framework for nanoparticle self-assembly*," Nano Letters 3 (10): 1341-1346 OCT 2003. [2] C.R. Iacovella, A.S. Keys and S.C. Glotzer, preprint. [3] C.R. Iacovella and S.C. Glotzer, " *Complex crystal structures formed by the self assembly of di-tethered nanospheres*," Nano Letters 9 (3), 1206-1211(2009). [4] C.R. Iacovella and S.C. Glotzer, "*Phase behavior of ditethered nanospheres*," Soft Matter 5 (22), 4492-4498 (2009).

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Cracking the code of nanoparticle self-assembly: An experimental and simulation study

Chakra Prasad Joshi$^{(1)}$*, chakraprasadjoshi@yahoo.com, 2801 W. Bancroft st, Toledo OH 43606, United States ; Yevgen Kryukov*$^{(2)}$*; Jacques G Amar*$^{(2)}$*; Terry P Bigioni*$^{(1)}$*. (1) Department of Chemistry, The University of Toledo, Toledo OH 43606, United States (2) Department of Physics and the Wright Center for photovoltaics innovation and commericalization, The University of Toledo, Toledo OH 43606, United States*

Cracking the code of nanoparticle self-assembly: An experimental and simulation study **C. P. Joshi[1], Y. Kryukov[2], J. G. Amar[2], and T. P. Bigioni[1]** [1]Department of Chemistry, [2]Department of Physics and Astronomy, and the Wright Center for Photovoltaics Innovation and Commercialization, The University of Toledo, Toledo, OH 43606 Self-assembly has immense potential for future technologies. Although interactions between large colloidal particles have been explained by DLVO theory, theories describing the interactions between nanoparticles are limited. Here, we attempt to further develop these theories by applying epitaxial theories to describe the self-assembly of 6 nm dodecanthiol-passivated Au nanoparticles on the 2D liquid-air interface of a drying drop. Colloidal nanoparticles self assembling by this mechanism are known to form high quality 2D monolayers in a way that is analogous to epitaxial growth. For example, plots of the island-size distribution and island density vs. D/F are consistent with a critical nucleus size of about $i = 5$. Solubility measurements showed that the nanoparticle-nanoparticle interaction through solvent was $DH = 7.1$ kJ/mol, or $-3.2\ k_BT$, which is consistent with the critical nucleus size measurements. These initial experiments point to the validity of this approach.

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Molecular dynamics simulations of DNA-based assembly of materials

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Surfaces functionalized with ssDNAs can be used to uniquely and reversibly bind complimentary DNAs. Such DNA modified materials are used in nanoscale supramolecular assembly, as optical, electrochemical and piezoelectric biosensors. Recognition and recombination pathways of DNA functionalized system are regulated by ssDNA hybridization. We conducted molecular dynamics simulation studies of DNA strands thiolated on the surface and in the presence of duplex and compared their dynamics to the dynamics of the DNA strands in solution. We investigated the optimal ssDNA length, effect of linker type and length to understand the effect of immobilization on subsequent DNA hybridization. Our results indicate that sensitivity and selectivity are directly dependent on the length and sequence of ssDNA strands. Our study helps understanding the science associated with the ssDNA hybridization and provides feedback to the associated experiments.

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Design of patchy particles using self-assembled monolayers

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Computational studies have shown the formation of patterns in a binary mixture of immiscible surfactants adsorbed on the surface of a spherical nanocolloid [1]. The resulting patterns (Janus, patches, and stripes) were in good agreement with experimental results [2]. Here we perform dissipative particle dynamics (DPD) simulations to study the patterns obtained by increasing the number of surfactants in the monolayer. These simulations resulted in a variety of new patterns that can be produced through different combinations of simple design elements, like nanocolloid size, degree of surfactant immiscibility, stoichiometry of the mixture, and length difference between surfactants. In all cases, the formation of patterns is driven by entropic gains at phase boundaries. [1] C. Singh et al. Physical Review Letters 99, 226106 (2007) [2] A. Centrone et al. Small 3, No. 5 (2007)

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Self-assembly of mixtures of nanorods in binary, phase-separating blends

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Aligned nanorod inclusions have the potential to significantly improve both the photovoltaic and mechanical properties of polymeric materials. Establishing facile methods for driving or “corralling” the nanorods to self-assemble into such aligned morphologies could facilitate the fabrication of effective, robust devices. Using a variety of computational methods, we model the self-assembly of a mixture of *A*-coated and *B*-coated rods in an *AB* phase-separating blend. Using dissipative particle dynamics (DPD) simulations, we first show that the steric repulsion between ligands causes the coated rods to preferentially align end-to-end within the minority phase of the binary blend. Using this information, we then utilize a coarse-grained approach, which combines a Cahn-Hilliard (CH) model for the polymer blend with a Brownian dynamics (BD) simulation for the rods, to simulate a larger sample of a rod-filled 30:70 *AB* thin film. We find that just a small volume fraction of *B* rods in the majority *B* phase promotes the percolation of *A*-like rods within *A*, so that the percolation threshold for the *A*-rods is significantly lowered. If, however, the number of *B* nanorods in the *B* phase exceeds a particular volume fraction, the *B* particles inhibit the percolation of the *A* rods. Thus, there is optimal volume fraction of *B* nanorods that provides the beneficial effects. The output from these morphological studies then serves as the input to the lattice spring model (LSM) for mechanical behavior of the composite. The results reveal that nanorods oriented along the tensile direction contribute to the enhancement of the macroscopic mechanical properties of the material. This multi-scale approach, integrating techniques that cover the microscopic, mesoscopic and macroscopic, provides a valuable means of determining structure-property relationships in nanocomposites and establishing useful guidelines for tailoring the components to yield optimal materials' properties.

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Understanding ligand distributions in modified particle and particlelike systems

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Chemical modification of nanoparticles or particle-like systems is ubiquitously being used in order to facilitate specific pharmaceutical functionalities or

physicochemical attributes of nanocrystals, proteins, enzymes or other particle-like systems. Often the modification process is incomplete and the functional activity of the product depends upon the distribution of functional ligands among the different particles in the system. Here, the distribution function describing the spread of ligands in particle-like systems undergoing partial modification reactions is derived and validated against a conjugated enzyme model system using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF). The distribution function is shown to be applicable to describe the distribution of ligands in a wide range of particle-like systems (such as enzymes, dendrimers or inorganic nanocrystals) and is used to establish guidelines for the synthesis of uniformly modified particle systems even at low reaction efficiencies.

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Grafting density effect on ionic screening around functionalized nanoparticles

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Recent investigations have revealed the remarkable enhanced stability of DNA-functionalized nanoparticles in cytosol as compared to molecular DNA [1]. Although an increased association was observed between nucleases and nanoparticle-grafted oligonucleotides, the degradation by enzymatic hydrolysis was observed to be inhibited, leading to an unexpected extension of DNA half-life within a cellular environment. We investigate the local ionic environment around DNA-functionalized nanoparticles as a responsible candidate, by means of classical density functional theory and molecular dynamics simulations. For varying grafting density and length of the oligonucleotides, we quantify the local density and composition of the ion cloud, and discuss the possible effects on the enzymatic activity of DNase I and related nucleases. Within a similar theoretical framework that significantly extends beyond the validity of conventional Debye-Huckel theory [2], we identify strong cohesive forces between nanoparticles induced by ion correlations. We observe the formation of ion bridges that tightly glue neighboring particles, which may enhance aggregation in addition to the effect of Van der Waals-forces, and discuss the importance for suspension stability and recognition. [1] D. S. Seferos, A. E. Prigodich, D. A. Giljohann, P. C. Patel, and C. A. Mirkin, Nano Lett. 9 (2009), 308-311 [2] J. W. Zwanikken, and M. Olvera de la Cruz **“Towards a quantitative theory for correlated electrolytes”** (submitted)

COLL 532

Biomolecular surfaces for the study and manipulation of circulating tumor cells

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Invasive cancer cells detach and migrate to new sites to initiate de novo tumors via the bloodstream, into which typically ~10^6 cells are released per gram of tumor tissue per day. These cells are believed to interact and adhere with the blood vessel wall through a multistep cascade with each step involving distinct receptors. We have successfully recreated this process by perfusing human cancer cell lines through microtubes functionalized with combinations of adhesion receptors. In addition to comparing the adhesion of different cancer cell lines to make predictions of relative metastatic potential, we have discovered that some types of cancer cells such as retinoblastoma stem cells must associate with circulating white blood cells as a precursor to adhesion with the vessel wall. Mimicking microvessels where tumor cells tend to engraft, combined molecular surfaces of selectins and other proteins have also been used to isolate rare tumor cells from patient blood samples. Coatings of silica nanoparticles or halloysite nanotubes were found to significantly enhance these cell capture processes under flow. Finally, we have developed two therapeutic applications that utilize biomimetic cell adhesion under flow to neutralize or reprogram tumor cells in the bloodstream. In the first approach, we co-immobilize adhesive selectin protein onto a device surface with TRAIL, a ligand that induces apoptosis (programmed cell death) in most types of cancer cells. As tumor cells are captured from flow and slowly roll across the surface of the device, they accumulate the TRAIL signal and die 1-2 days after exiting the device. Alternatively, we have encapsulated siRNA into nanoscale liposomes functionalized with adhesion receptors, to target circulating tumor cells through these same rolling interactions.