SYMPOSIUM H

H: Biological and Bio-Inspired Materials Assembly

December 1 - 2, 2003

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* Invited paper

SESSION H1
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Monday Morning, December 1, 2003
Back Bay B (Sheraton)

8:30 AM *H1.1
Structural DNA Nanotechnology. Nadrian C. Seeman, Chemistry, New York University, New York, New York.

Structural DNA nanotechnology uses reciprocal exchange between DNA double helices or hairpins to produce branched DNA motifs, like Holliday junctions, or related structures, such as double crossover (DX), triple crossover (TX), paranemic crossover (PX) and DNA parallelogram motifs. We combine DNA motifs to produce specific structures by using sticky-ended cohesion. The strength of sticky-ended cohesion is that it produces predictable adhesion combined with known structure. From simple branched junctions, we have constructed DNA stick-polyhedra, such as a cube and a truncated octahedron, several deliberately designed knots, and Borromean rings. We have used two DX molecules to construct a DNA nanomechanical device by linking them with a segment that can be switched between left-handed Z-DNA with right-handed B-DNA. PX DNA has been used to produce a robust sequence-dependent device that changes states by varied hybridization topology. A central goal of DNA nanotechnology is the self-assembly of periodic matter. We have constructed micron-sized 2-dimensional DNA arrays from DX, TX, DX triangle and DNA parallelogram motifs. We can produce specific designed patterns visible in the AFM from DX and TX molecules. We can change the patterns by changing the components, and by modification after assembly. In addition, we have generated 2D arrays from DNA parallelograms. These arrays contain cavities whose sizes can be tuned by design. In studies complementary to specific periodic self-assembly, we have performed algorithmic constructions, corresponding to XOR operations. The key challenge in the area is the extension of the 2D results obtained so far to 3D systems. We expect to be able to produce high resolution crystals of DNA host lattices with heterologous guests, leading to well-ordered bio-macromolecular systems amenable to diffraction analysis. Other challenges are to incorporate DNA nanomechanical devices in periodic and aperiodic lattices and to use the lattices to organize nanoelectronic components. Self-replicating structural systems present a further exciting avenue to be pursued. Biology contains numerous lessons for the physical sciences. The existence of living systems with nanoscale structural components represents an existence proof that autonomous systems can build up and function on this scale, systems capable of energy transduction and replication. The overall challenge that biology presents to the physical sciences is to move from biokleptic to biomimetic to abiological systems that perform in this same manner. Supported by grants from NIGMS, ONR, NSF and DARPA/AFOSR.

9:00 AM *H1.2
DNA-directed assembly on dual-functionalized microspheres. Manish Bajaj[1] and Paul E Laibinis[2]; [1]Chemical Engineering, MIT, Cambridge, Massachusetts; [2]Chemical Engineering, Rice University, Houston, Texas.

The bottom-up assembly of functional devices requires novel building blocks to facilitate the incorporation of functional and structural hierarchy. Anisotropic building blocks can substantially broaden the creation of self-assembled devices with unique properties because of the morphological and/or chemical asymmetry. In this regard, we have created microspheres with one hemispherical face exposing silica and the other exposing gold. These microspheres were formed by the shadow deposition of gold onto silica microspheres. The two different surfaces allowed the use of different surface chemistries – silane chemistry for the silica side and thiol chemistry for the gold side – to immobilize different oligo sequences on the two faces. These dual-functionalized microspheres were used for the selective orthogonal assembly of fluorophore-tagged target oligonucleotides. This DNA-directed assembly was confirmed by confocal microscopy of the microspheres. We have also used the unique recognition capabilities of DNA molecules to assemble gold nanoparticles of different sizes on the two sides of the dual-functionalized microspheres. In essence, employing DNA as the linker molecule, these 'Janus' particles can be assembled into various novel 1-D, 2-D, and 3-D structures, which are difficult to realize using symmetrical building blocks.

9:30 AM *H1.3
Biomolecular Functionalization and Organization of Nanoparticles. Christof M. Niemeyer, Uni Dortmund, Dortmund, Germany.

We have developed self-assembled oligomeric networks consisting of streptavidin (STV) and dsDNA, which are applicable as model systems for ion-switchable nanoparticle networks and nanometer-scaled "soft material" standards for scanning probe microscopy. Moreover, conjugates of single-stranded DNA and STV have been utilized as biomolecular adapters for the immobilization of biotinylated macromolecules at solid substrates via nucleic acid hybridization. This "DNA-directed immobilization" allows one for reversible and site-selective functionalization of solid substrates with metal and semiconductor nanoparticles, or, vice-versa, for the DNA-directed functionalization of gold nanoparticles with proteins, such as immunoglobulins and enzymes. This approach is applicable for the detection of chip-immobilized antigens. Moreover, the covalent DNA-STV conjugates allow for selective positioning of biotin-derivatized components along a single-stranded nucleic acid molecule. Examples include the fabrication of functional biometallic nanostructures from gold nanoparticles and antibodies, applicable as diagnostic tools in bioanalytics.

10:30 AM *H1.4
Helical and Random Coil Protein Scaffolds for Building Designer Macromolecules. Robin S. Farmer[1,2], Brian D. Polizzotti[1,2] and Kristi L. Kiick[1,2]; [1]Department of Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Delaware Biotechnology Institute, Newark, Delaware.

We are capitalizing on the structural and sequence control of protein biosynthesis, combined with the novel chemical reactivity of non-natural amino acids, to create new polymeric materials with exceptional architectural control and targeted function. There are various areas we are exploring in which such macromolecules could be uniquely useful, including the presentation of saccharides, peptides, photoactive groups, and electronically active molecules. Our initial research has focused on the controlled presentation of saccharides, as multivalent protein-saccharide binding events mediate many biological processes such as inflammation, toxin pathogenesis, and metastasis. Although it is known that the nature of the scaffold and the number and spatial distribution of saccharides are critical in controlling binding, these variables cannot be controlled simultaneously in synthetic polymers. Therefore, we have produced a series of artificial proteins, helical and random coil, in which the position of glutamic acid residues has been varied systematically; these sites provide points for attachment of saccharides. Alanine-rich helical polymers have been designed to present glutamic acid residues on a helical face with a distance between glutamic acids of approximately 17, 35, and 65 angstroms; these distances are commensurate with receptor spacing of a variety of toxins and lectins. Proteins from this family are easily expressed from *E.coli* and are highly helical over a range of pH values and temperatures. Glutamic-acid containing random coil peptides and proteins have also been synthesized by both solid-phase and genetically directed methods. These molecules can be readily modified with saccharides to yield artificial glycopeptides and glycoproteins, and the binding of these molecules to relevant toxins, such as the cholera toxin, has been investigated by immunochemical assays. We have also started to explore the chemistry of non-natural amino acids in order to create protein scaffolds decorated with saccharides and other molecules; recent progress in these areas will also be briefly discussed. These polymers have enormous potential not only in the construction of novel toxin inhibitors and cell signaling activators, but also in the design of macromolecules for other materials and device applications.

11:00 AM *H1.5
Chemical Self-assembly of Textured Peptide Tapes with Nanoscale Order. Regina Valluzzi[1], Hyoung-Joon Jin[2,1] and Jacco van Beek[3,1]; [1]Chemical and Biological Engineering, Tufts University, Medford, Massachusetts; [2]Chemistry, INHA University, Incheon, South Korea; [3]Chemistry, University of Sheffield, Sheffield, United Kingdom.

Multilayered amorphous mm to cm long "tapes" can be obtained as precipitates from several designed peptides with amphiphilic sequences. Acid blocks on the ends of the peptide sequences have been used to functionalize the "tapes" with inorganic ions. The peptide tapes are self-limiting in width and thickness, but grow lengthwise to form long coils. A hierarchical, or multiscale, pattern of undulations and ridges is observed on the surface of the tapes, and is correlated to the birefringence observed for the tapes. This suggests a structural origin for the texture - molecular or cluster orientation - rather than a purely topographic or environmental origin. Even though the sequences are looslely based on silks, and "silk-like" crystal structures have been obtained for these molecules under different conditions, no silk-like crystal structures are observed in the tapes. FTIR data suggest a "silk I"-like secondary structure. Strong X-ray scattering at positions corresponding to several nanometers suggests a folded structure, arranged in layers. Evidence for chiral layers (a solid version of a chiral smectic phase) is observed in high resolution SEM. The folded supersecondary structure suggested by these data tapes resembles the folded beta-sheet structures in amyloids, but the beta-strand conformation and crystalline local order are missing. The

occurrence of the tapes under conditions very close to those required for beta-sheet crystallization suggests a "trapped" precursor to the folded beta-sheet structure.

11:30 AM *H1.6
From Biomimetic Membranes to Active Materials.
Jacob Schmidt, Bioengineering, UCLA, Los Angeles, California.

We are developing a new family of active materials which derive their functional properties from membrane proteins. These materials have two primary components: the proteins and the membranes themselves. I will discuss our recent work directed toward development of a generic platform for a "plug-and-play" philosophy of membrane protein engineering. By creating a stable biomimetic polymer membrane a single molecular monolayer thick, we will enable the exploitation of the function of any membrane protein, from pores and pumps to sensors and energy transducers. Our initial work has centered on the creation, study, and characterization of the biomimetic membranes. We are attempting to make large areas of membrane monolayers using Langmuir-Blodgett film formation as well as through arrays of microfabricated black lipid membrane-type septa. A number of techniques allow the insertion of protein into the membranes. As a benchmark, we have been employing a model system of voltage-gated pore proteins, which have electrically controllable porosities. I will report on the progress of this work, the characterization of the membranes, protein insertion processes, and the yield and functionality of the composite. What we learn in this work is being applied to other proteins, such as the mechanosensitive channel protein MscL and the water-specific pore protein AqpZ, directed toward compact devices for mechanical sensing and water purification.

SESSION H2
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Monday Afternoon, December 1, 2003
Back Bay B (Sheraton)

1:30 PM *H2.1
Phenylene Ethynylenes as Amphiphilic Beta-Sheet Biomimetics. Greg Tew, university of mass-amherst, Amherst, Massachusetts.

New amphiphilic poly(phenylene ethynylene)s have been synthesized. These polymers have non-polar alkyl side chains and positively charged amines that extend from opposite sides of the backbone. The polymers have been shown to form monolayers at the air/water interface on a Langmuir trough with an estimated area per repeat unit of 45 square angstroms. This is important because many proteins have been shown to have an amphiphilic nature, a property that aids in membrane binding. In addition, these polymers are found to self-organize in aqueous solution into bilayers which resemble amphiphilic beta-sheets. The newly synthesized polymers have potential applications as antimicrobial agents and surface modifiers. In addition, their self-assembling properties are being explored.

2:00 PM *H2.2
Bio-inspired Synthesis and Solution Assembly of Linear-Dendritic Copolymers for Delivery Applications. Kris Stokes, Kris C Wood, Phuong Nguyen and Paula T. Hammond; Chemical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A large amount of knowledge has been obtained on the modification of spherical dendrimer systems for specific binding13-16, and their use as unimolecular micelles, with emphasis on drug delivery and encapsulation applications. In all cases, the size and functionality of these nano-delivery vehicles are limited by the size of the dendrimer; further, it is difficult to tune the density and functionality of groups without additional synthesis, which requires a great deal of synthetic effort and financial cost. By creating linear-dendritic block copolymers which can act as amphiphiles in solution, much larger nanostructures can be constructed through the formation of micelles containing N chain aggregates of dendritic species, while the high functional density of the dendrimer system is utilized more efficiently. The synthesis and the solution behavior of hydrophilic block poly(ethylene-oxide)-b-PAMAM and the hydrophobic polystyrene-b-PAMAM systems will be addressed as model systems of assembly behavior. Synthetic approaches for the incorporation of biocompatible blocks and targeting ligand will be discussed, as well as examples of gene/drug delivery using these designed macromolecule systems.

2:30 PM *H2.3
Synthetic Analogs of Natural Macromolecules: A General Approach to Biomimetic Polymers. Heather D. Maynard, Jungyeon Hwang, Joyce E. Sayegh and Sung Jung Hong; Department of Chemistry & Biochemistry, UCLA, Los Angeles, California.

Synthetic analogs of natural macromolecules, such as the extracellular matrix protein fibronectin, can serve as modulators of cellular processes. We have developed general synthetic strategies to provide rapid access to polymers of this description. For example, universal block copolymer scaffolds with sequences of orthogonally reactive groups have been prepared. Using this approach, many biopolymers with diverse functionality could be generated from a single polymer precursor, without the need to establish monomer and polymer synthesis conditions each time. This strategy should be valuable in the rapid creation of materials, for example, for drug delivery and sensors. Synthesis, characterization, and applications will be discussed.

3:30 PM *H2.4
Bio-inspired Self-Assembly Approaches to Multifunctional Hybrid Materials. Ulrich Wiesner, Department for Material Science and Engineering, Cornell University, Ithaca, New York.

The study of polymer based self-assembly ("bottom-up") approaches to multifunctional polymer-inorganic hybrid materials is an exciting emerging research area interfacing solid state and soft materials and offering enormous scientific and technological promise. By choice of the appropriate synthetic polymers as well as ceramic precursors unprecedented morphology control down to the nanoscale is obtained. Tailoring of the polymer-inorganic interface is of key importance. The structures generated on the nanoscale are a result of a fine balance of competing interactions, a typical feature of complex biological systems. The potential for new multifunctional materials lies in the versatility of the polymer chemistry as well as that of the inorganic chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructued hybrid materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. In all cases cooperative self-assembly of organic and inorganic species is induced through blocked macromolecules. Besides amorphous and crystalline oxide materials novel systems toward high temperature SiCN and SiC structures are introduced. Examples will include the preparation of mesoporous materials and superparamagnetic mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis, solid hybrid polymer electrolytes for battery applications, the synthesis of nanoparticles with controlled shape, size, and composition for applications in the life sciences, as well as thin film materials with potential applications in microelectronics and nanobiotechnology.

4:00 PM *H2.5
Tethered Nanoparticles: A New Class of "Macromolecule" for Bio-Inspired Materials Assembly. Sharon C Glotzer[1,2], Zhenli Zhang[1], Charles (Xi) Zhang[2], Monica H Lamm[1], Mark A Horsch[1] and Elaine R Chan[1]; [1]Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan; [2]Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

An impressive variety of nano building blocks - including nanospheres, nanorods, nanocubes, nanoplates, nanotetrapods, and nanoprisms - exists and continues to grow with breakthroughs in synthesis techniques. Increasingly, synthetic chemists are turning their attention to the biomimetic functionalization of nano building blocks (both nanocrystals and supramolecular entities) to direct their self-assembly into complex structures for novel materials and devices. Inspired by these recent advances, we seek to develop an intuitive and general framework for predicting the assembly of nanoparticles functionalized at specific locations with oligomeric tethers or biomolecular "handles" into complex one-, two- and three-dimensional structures. In this regard, molecular simulation of model nano building blocks can yield insight into the conditions under which various structures may be achieved, and can be used to map out phase diagrams of assembled structures. As a first step toward this goal, we use molecular simulations to study the self-assembly of biomimetically functionalized nanocrystals (e.g. quantum dots) and nanostructured molecules (e.g. cubic silsesquioxanes and fullerenes) in solution. We show how tuning thermodynamic parameters and architectural features of model nano building blocks can control aspects of local and global ordering of the nanoparticles. We further demonstrate that for certain categories of these novel nano building blocks the simulated morphologies obtained emulate those occurring in natural systems and may be predicted using concepts from block copolymer microphase separation and liquid crystal phase ordering, while for other categories the unique packing constraints introduced by nanoparticle geometry and by building block topology lead to structures far richer than those found in conventional block copolymer, surfactant, and liquid crystal systems, including nanowires, nano-shells, nano-sheets, and nano-cylinders. Our results suggest the potential usefulness of considering tethered nanoparticles as a new class of "macromolecule" for bio-inspired materials assembly. This work is supported by grants from the

National Science Foundation (DMR-0103399 and CTS-0210551) and the U.S. Department of Energy (DE-FG02-02ER46000).

4:30 PM *H2.6
Synthesis and Single Molecule Studies of Titin Mimic Modular Polymers. Zhibin Guan, Jason T. Roland, Sharon X. Ma, Jane Z. Bai and Maianh Nguyen; Chemistry, University of California, Irvine, California.

Nature has evolved excellent materials renowned for their strength and toughness. Recent studies of some biopolymers suggest that these exceptional properties arise from a modular elongation mechanism involving noncovalent interactions and molecular self-assembly to create a well defined supramolecular structure. As an example, the muscle protein titin has been shown to have a modular structure comprised of a linear array of domains. Recent single molecule studies on the titin protein revealed that this modular structure is the key to achieving its combined strength and toughness. Natures elegant molecular mechanism inspired us to address a longstanding challenge in material science: how to create macromolecular materials with both high strength and toughness. Using titin as a model, a plan was devised to create synthetic macromolecules using multiple loops and domains to serve as modules, thereby creating materials with high fracture toughness and strength. The synthetic strategy adopted uses the strong, precise hydrogen-bonding motif 2-ureidon-4-pyrimidone (Upy) to direct the formation modular domains along a polymer chain. This presentation will discuss the synthesis, single-molecule studies, and bulk mechanical property studies of the titin-mimicking modular polymers.

SESSION H3: Poster Session I
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

H3.1
Chemoslective Ligation Methods for the Ordered Attachment of Virus and Proteins to Surfaces. Julio A. Camarero[1], Chin Li Cheung[1], Bruce W. Woods[1], Tianwei Lin[2], John E. Johnson[2] and James J. De Yoreo[1]; [1]Lawrence Livermore National Laboratory, Livermore, California; [2]The Scripps Research Institute, La Jolla, California.

The present work describes our ongoing efforts towards the creation of micro and nano-scaled ordered arrays of protein/virus covalently attached to site-specific chemical linkers patterned by different nano- and microlithograpic techniques. We will present a new and efficient solid-phase approach for the synthesis of chemically modified long alkyl-thiols. These compounds can be used to introduce chemoselective reacting groups onto gold and silicon-based surfaces. We will showt that these modified thiols can be used for creating nano- and micrometric chemcial patterns by using different lithography techniques. We will show that this patterns can react chemoselectively with proteins and virus which have been chemically or recombinantly modified to contain complementary chemical groups at specific positions thus resulting in the oriented attachment of the protein or virus to the surface. Also a total novel and generic approach for the chemoenzymatic and photoswitchable attachment of proteins to surfaces will be presented.

H3.2
SPR Imaging Measurements of Bioaffinity Interactions Using Peptide, Protein, and DNA Arrays Fabricated on Gold Thin Films. Greta Wegner, Hye Jin Lee and Robert Corn; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

Surface plasmon resonance (SPR) imaging has emerged as a powerful tool for the study of bioaffinity interactions using a surface array format. SPR imaging is a label-free technique used to monitor the adsorption of biomolecules to a chemically modified gold thin film by measuring changes in the local index of refraction. Peptide, protein, and DNA arrays have been fabricated using microfluidic channels constructed in polydimethyl siloxane (PDMS). A variety of bioaffinity interactions have recently been studied using SPR imaging measurements including (a) antibody-epitope adsorption using peptide arrays, (b) protein-protein and protein-DNA interactions using arrays of his-tagged fusion proteins, and (c) enzymatic modification kinetics of DNA and peptide by proteases and resolvases for mutation analysis.

H3.3
Abstract Withdrawn

H3.4
Functional Membrane Mimetics on Solid Support. Edwin Li and Kalina Hristova; Materials Science, Johns Hopkins University, Baltimore, Maryland.

The plasma membrane, located at the interface between the cell and the environment, mediates vital biochemical processes, such as signal transduction, nutrients transport, electrical excitability, adhesion and molecular recognition. Therefore, the biotechnological potential of fully functional membrane mimetics on solid support is enormous. Lipid-only membranes have been successfully assembled on solid support. The current challenge is control over orientations and lateral mobility of the incorporated membrane proteins. We have assembled membrane mimetics consisting of (1) surface-attached lipid bilayers and (2) reconstituted membrane proteins that conduct biochemical signals via lateral dimerization in the bilayer plane. Protein mobility is assessed using fluorescence recovery after photobleaching (FRAP). The dimerization of the freely diffusing, fluorescently labeled proteins is measured using fluorescence resonance energy transfer (FRET). FRET provides quantitative information about the dimerization propensity of the proteins. This work will lay the foundation for the development of novel biomimetic systems for the study of cell signaling across the plasma membrane. It will also pave the way to the fabrication of devices that can detect pathogenic membrane protein mutations and identify therapeutic agents. Supported by Whitaker RG-01-0370.

H3.5
AFM / SEM Investigation of Nano to Micron Scale Structures Formed on Gold during Enzymatic Copolymerization of the Biomimetic Monomers- Amphiphilic Decyl Ester of L-Tyrosine and Tyrosineamide. Jun Seok Lee[1], Changmo Sung[1], Kyoung Sung Oh[2] and Kenneth A Marx[3]; [1]Center for Advanced Materials, University of Massachusetts, Lowell, Massachusetts; [2]Department of Chemistry, University of Massachusetts, Lowell, Massachusetts; [3]Center for Intelligent Biomaterials, University of Massachusetts, Lowell, Massachusetts.

The pure amphiphilic decyl ester of L-tyrosine (DELT) and DEDT (D-isomer) monomers above their cmc each form long rod- shaped aggregates ($\sim$10s μm) 2-3 microns in diameter. Diameters were unchanged following enzymatic polymerization but their stable lengths increased ($>$ 100 μm) following polymerization (1). These self-assembling monomers bind the gold Quartz Crystal Microbalance (QCM) surface at increasing pH (2), and can be electropolymerized at gold and Pt QCM electrode surfaces (3). We followed the course of enzymatic polymerization in these optically opaque solutions via QCM parameters that resulted from increases in the aggregates viscoelastic properties during polymerization (2). In the current study, we copolymerized two monomers, DELT (below its cmc) and tyrosineamide- both derivatives of the amino acid tyrosine, in a 1:1 molar ratio (both 0.3 mM) with horseradish peroxidase and hydrogen peroxide, in buffered solution. Gold coated mica substrates were immersed in the solution immediately before copolymerization began and the resulting oligomers adsorbed to the gold coated substrates in a time dependent fashion for varying times up to 30 hr after the initiation of polymerization. Using XPS measurements of an independent set of gold coated substrates, the surface of the gold was found to be completely covered by 24 hr, in agreement with previous work (4). When examined with SEM and AFM at 24 hr, irregular spherical aggregates below and above 1 μm diameter were observed bound to the gold covered mica substrates. With AFM, we observed that these spherical aggregates grew from much smaller nanoscale aggregates early in the polymerization process to a point where bead density was tightly packed. The copolymerized structures were more regular when compared to the unpolymerized mixture of monomers that formed similar but less regular spherically shaped and sized structures on the surface. The copolymerized structures also attained a measured surface roughness that was 4-fold greater and a mean height that was 7-fold greater than the unpolymerized monomer mixture. These results agree with the behavior observed for DELT above its cmc in the QCM experiments that we already discussed (2). 1. Marx, K.A., Alva, K.S. and Sarma, R., Mater. Sci. & Eng. C **11**, 155-163 (**2000**). 2. Marx, K.A., Zhou, T and Sarma, R., Biotech. Prog., **15**, 522-528 (**1999**). 3. Marx, K.A. and Zhou, T., J. Electroanal. Chem., **521**, 53-60 (**2002**). 4. Angelopoulos, A., Marx, K.A., Oh, K.S., MRS Proc., **710**, 207-212 (**2002**).

H3.6
Abstract Withdrawn

H3.7
Steps Toward *Ex – vivo* Collagen Synthesis. Sergey E Paramonov and Jeffrey D. Hartgerink; Chemistry, Rice University, Houston, Texas.

Collagen is the major component of almost any connective tissue in a multicellular organism. The structure of collagen is represented by a triple helix, which consists of three left-handed poly(proline-II)-like

chains. The chains are wound around one another forming a right-handed superhelix. The primary structure of collagen single chains consists of repeated trimer units Gly-X-Y, where a large proportion of X residues are proline and a large proportion of Y residues are hydroxyproline. Typical collagen fiber contains over 1000 residues and can range over 3000$\AA$. Being the most abundant protein in extracellular matrix collagen presents a tempting target for a new generation of biomimetic materials. $Ex - vivo$ synthesis of collagen offering control over its chemical signals may bring the area of tissue engineering to a new level of sophisticating. Unfortunately, sufficiently long collagen fibers cannot be synthesized by the usual solid phase peptide synthesis (SPPS), so other synthetic routs must be found. Here we suggest an approach, which utilizes principles of supramolecular chemistry such as self-assembly and self-organization. First relatively short (21 aa) peptides containing native collagen motif were synthesized by SPPS. Oppositely charged amino acids Glu and Lys were incorporated into the sequences at distinct places in order to force the staggered self-assembly of the peptides. This design allows the triple helical structure to propagate in a supramolecular polymerization. Native ligation technique will be used to covalently link the free terminii of each triple helix with one another. This covalent capture will help to maintain strength along the self-assembled triple helix, and provide nucleophilic attachment sites (cysteine side chains) for further collagen modifications. The system has been characterized by CD, IR spectroscopy and transmition electron microscopy.

H3.8

Exploring Molecular Diversity of Repetitious Artificial Proteins Created by a "Frame Shuffling" Method.

Kenji Kashiwagi[1,2] and Kiyotaka Shiba[1,2]; [1]Protein engineering, Cancer Institute, Japanese Foundation for Cancer Research, Toshima, Tokyo, Japan; [2]CREST, Japan Science and Technology Corporation, c/o Cancer Institute, Japanese Foundation for Cancer Research, Toshima, Tokyo, Japan.

We have established a novel protein creation system, MolCraft, in which repetitious proteins are created through polymerization of a designer microgene (PNAS 94:3805, 1997). Artificial proteins created by this method often show properties of self-assembly (Protein Engn. 16:57, 2003) or self-organization (EMBO Reports 4:148, 2003), which are attractive properties for protein-based materials. To explore the potential of the MolCraft system in the material science field, we have developed a new method that can increase the molecular diversity of the proteins created from MolCraft. In a standard MolCraft protocol, polymers of a microgene, which is devoid of the termination codon in any one of its three reading frames, is prepared by the microgene polymerization reaction (MPR) method. In MPR, nucleotide insertions or deletions randomly occur at junctions of the microgene units, resulting in the random transfer of translational frames at the junctions. Proteins created from a standard MolCraft, therefore, are combinatorial polymers of three peptides that are coded from a single microgene. To increase the molecular diversity of the microgene polymers in a newly established protocol, the microgene polymers are further mutated using a Y-family DNA polymerase. Because the Y-family DNA polymerase is known to introduce nucleotide deletion or insertions in its polymerization reaction, the PCR-amplified products with a Y-family DNA polymerase have frame shift mutations at high rates. By taking advantage of this unique character of the Y-family DNA polymerase, we can increase the frequencies of the frame changes in the microgene polymers, thus giving greater molecular diversities to the repetitious proteins. We called this new method "frame shuffling". In our poster, we also describe the physico-chemical properties of the proteins created by this "frame-shuffling" method.

H3.9

A Study of the Self-Assembling Morphology in Peptide Nanorings and Nanotubes.

Hajime Okamoto[1], Tsutomu Nakanishi[1], Yukiko Nagai[1], Tetsuo Yamada[1], Hiroshi Miyazaki[1], Kyozaburo Takeda[1], Yukio Furukawa[2], Ikuo Obataya[3], Hisakazu Mihara[3], Hiroaki Azehara[4], Wataru Mizutani[4], Katsushi Hashimoto[5,6], Hiroshi Yamaguchi[5] and Yoshiro Hirayama[5,6]; [1]Department of Materials Science and Engineering, Waseda University, Shinjyuku, Tokyo 169-8555, Japan; [2]Department of Chemistry, Waseda University, Shinjyuku, Tokyo 169-8555, Japan; [3]Department of Bioengineering, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8501, Japan; [4]Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8562, Japan; [5]NTT Basic Research Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan; [6]CREST-JST, Saitama 331-0012, Japan.

Recently, numerous biological supramolecules have been artificially synthesized using the process of self-assembling. Scientists have mimicked the spontaneous formation of biopolymers and fabricated tailor-made biomolecules at nano-scale. The peptide nanotube is one of those exciting nano-biomaterials constructed by the self-assembly of peptide nanorings[1]. Because the number and kind of amino acids are adjusted artificially, both the internal diameter and surface property can be controlled at will. Therefore, the peptide nanotube is expected to have a wide range of potential applications in, for example, medicine, chemistry, materials science. Several important experiments and theoretical works have been carried out to study the electronic and molecular structures of peptide nanotubes[2,3]. However, to go one step further and apply them in various areas, one should strive to understand and control their intimate self-assembling morphology. Especially, to comprehend how the difference in the number or kind of amino acids changes their morphology is crucial. Thus, we here target four peptide nanotubes of cyclo[-(D-Ala-L-Gln)$_4$], cyclo[-(D-Ala-L-Gln)$_3$], cyclo[-(D-Cys-L-Gln)$_3$] and cyclo[-(L-Gln)$_5$], and study their self-assembling forms by scanning probe microscopy. For this purpose, we first synthesized the above four peptides by the Fmoc solid-phase method and identified them by mass spectrometry and FT-IR spectroscopy. Successively, we carried out the atomic force microscopy and observed their several interesting self-assembling forms on gold or mica substrates. The resulting images of the former three DL-peptides showed not only their straight tubular forms but also some bundles of these nanotubes. The number and size of the observed bundles were rather different among those three peptides, and we discussed such difference based on our theoretical consideration. In contrast to the DL-peptides, the resulting image of cyclo[-(L-Gln)$_5$] showed the meandering nanotubular form. This meandering nature is supported by our *abinitio* calculations, which reveal that the symmetry lowering in the five-membered ring (C_1) causes the meandering ring stacking. We, moreover, succeeded in observing a super-ring form of the nanotubes (about 200 nm in diameter) and also the nanotube-growing on the substrates. These interesting forms can be considered to come from the meandering nature of the cyclo[-(L-Gln)$_5$] nanotube. In addition to the atomic force microscopy, we performed the scanning tunneling microscopy and obtained the high-resolution images of the single peptide nanotubes (about 2 nm in width) as well as the nanotube bundles. These results will pave the way for a molecular manipulation and application of the peptide nanotubes. [1] M. R. Ghadiri et al.; Nature 366 (1993) 324. [2] D. T. Bong et al.; Angew. Chem. Int. Ed. 40 (2001) 988. [3] H. Okamoto et al.; J. Am. Chem. Soc., 125 (2003) 2756.

H3.10

Artificial Glycopolypeptides for the Inhibition of Bacterial Toxins.

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Inhibition of the binding of toxins or pathogenic organisms to the saccharides on mammalian cell surfaces is a potentially attractive therapeutic strategy. Toxins and pathogens achieve highly efficient and selective binding through multivalent interactions facilitated by relevant oligosaccharide structure as well as by the presence of multiple saccharide receptors per toxin/pathogen subunit. Although the importance of the number and spacing of saccharides on a scaffold is known to be critically important in binding to multivalent receptors, it has been essentially impossible to synthesize synthetic polymer architectures that exhibit control over both variables. In our investigations, we aim to synthesize a family of artificial glycoproteins in which both spacing and number of saccharides are controlled. As a first step, we have investigated a series of random coil glycopeptides with regularly spaced saccharide ligands as inhibitors of the cholera toxin. The cholera toxin, a member of the AB5 bacterial toxin family, gains entry into the mammalian cell only after recognition of the GM1 ganglioside on the mammalian cell by the B5 homopentamer of the toxin. The spatial arrangement of the binding sites on the B5 subunit provides an excellent model for the structure-based design of multivalent ligands. Polypeptides displaying glutamic acid side chains at regular intervals were synthesized by solid-phase techniques and genetically directed methods. The peptides were glycosylated with amino-functionalized saccharides via HBTU-activated coupling chemistry and purified by high performance liquid chromatography (HPLC). The complete derivatization of the glycopeptides was confirmed by nuclear magnetic resonance spectroscopy (NMR) and matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI TOF). The potential for these glycopeptides and glycoproteins as high-affinity inhibitors of the cholera toxin was tested by competitive enzyme-linked immunosorbent assay (ELISA). These investigations are not only of interest for the design of efficient glycopeptide toxin inhibitors, but will also aid in the deconvolution of the impact of multivalency, spacing, and backbone rigidity in a variety of other biologically relevant binding events.

H3.11

Design and Synthesis of Helical Protein Polymers for Controlled Presentation of Multiple Ligands.

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Multivalent protein-saccharide binding events play a prominent role in directing biological processes such as the immune and inflammatory responses and bacterial pathogenesis. Although a variety of synthetic glycopolymers have shown improved binding, relative to monosaccharides, to targets such as lectins, viruses, and cell surface receptors, the underlying importance of saccharide number, saccharide spacing, and backbone conformation in the binding event cannot be fully explored or optimized with these heterogeneous polymers. Therefore, a family of artificial proteins has been designed and produced by genetically directed methods to permit the study of the effect of ligand spacing, ligand number, and protein conformation on binding events. Here we report the genetically directed synthesis of alanine-rich proteins with the general composition $[AAAQAAAEAAAQ]_x$. Variations in this monomer sequence allow specification of the spacing between glutamic acid residues, which provide chemically reactive sites for the attachment of ligand molecules, such as saccharides or small peptides, along the protein backbone. Three different 'monomer' sequences were designed to yield functional group spacings of approximately $17\AA$, $35\AA$, and $65\AA$; these distances are commensurate with receptor spacings of a variety of toxins and lectins. Protein polymers comprising these monomers were expressed from E. coli, and the proteins were characterized by HPLC, MALDI-TOF, and amino acid analysis to confirm their composition. Circular dichroism spectroscopy shows that the proteins are highly helical over a range of pH values and temperatures, as expected for alanine-rich sequences. Because of the potential control over ligand spacing, these proteins are excellent candidates for studies aimed at determining the effect of ligand spacing and number on binding. The α-helical conformation of the alanine-rich proteins adds a new dimension to such investigations by introducing the effect of backbone conformation on the ligand-receptor interaction. These novel polymers therefore have enormous potential for mediating protein binding and cell signaling events.

H3.12
InVivo **Incorporation of Fluorinated Amino Acids into Proteins.** Soojin Son, Pin Wang and David A Tirrell; Division of Chemistry & Chemical Engineering, California Institute of Technology, Pasadena, California.

Protein biosynthesis using traditional recombinant DNA technology confines us to the incorporation of the 20 naturally occurring amino acids and the limited functionality that they provide. In an effort to expand the versatility of protein engineering, nonnatural amino acids have been incorporated *invivo*, a process that can alter the biological, chemical, and physical properties of biopolymers. Recently, 5,5,5-trifluoroisoleucine (5TFI) and 4,4,4-trifluorovaline (4TFV) have been incorporated into a model target protein in an isoleucine/valine auxotrophic E. coli host strain grown in 5TFI or 4TFV-supplemented minimal medium, respectively. Residue-specific incorporation of 5TFI and 4TFV has been confirmed to be over 90% complete as evidenced by MALDI-MS and amino acid analysis. Previously, fluorination has been demonstrated to enhance thermal and chemical stabilities of proteins, such as in the case of trifluoroleucine incorporation in the hydrophobic cores of leucine-zipper peptides. In light of this result, we are investigating the stabilizing effects of 5TFI and 4TFV incorporation into mutant leucine-zipper peptides derived from the yeast transcription factor GCN4. Effects of fluorination are also being explored in the context of oligomerization states and DNA binding activity of these mutant *bzip* peptides.

H3.13
Micro-Nano Structure and Viscoelastic Properties of Hydrogels Formed Via Intramolecular Folding and Self-Assembly of Amphiphilic β-Hairpin Molecules. Bulent Ozbas[1], Karthikan Rajagopal[2], Lisa Pakstis[1], Matthew S Lamm[1], Juliana Kretsinger[2], Lisa Haines[2], Joel P Schneider[2] and Darrin J Pochan[1]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Chemistry and Biochemistry, University of Delaware, Newark, Delaware.

Here we studied the formation of hydrogels via the intramolecular folding and consequent self-assembly of 20 aminoacid long β-Hairpin peptide molecules. These hairpin molecules are amphiphilic in nature with an alternating sequence of hydrophobic valine and hydrophilic lysine amino acids surrounding a tripeptide turn sequence. These molecules are found to form hydrogels at low peptide concentrations ($\sim$1 wt%) rich in β-sheet secondary structure due to intramolecular folding induced at either high pH ($\sim$9), high salt concentration ($\sim$150 mM), or temperature jumps. The effects of β-Hairpin molecule chemistry (arm sequence and β-turn), and solution conditions on the structure and viscoelastic properties are discussed. The micro- and nano-structure of the self-assembled hydrogels are studied by laser scanning confocal microscopy, transmission electron microscopy, and neutron and x-ray scattering. At the microscale, hydrogel structure is heterogeneous with water channels in the order of 10 μm. The self-assembled regions consist of interconnected fibrillar/tubular networks. The viscoelastic properties of the hydrogels are measured by dynamic oscillatory rheology measurements. Kinetics of gel formation is studied to understand the effects of peptide sequence on folding and self-assembly and consequent gelation. The storage moduli ($G\prime$) are on the order of kPa at low concentration of peptide ($<$3 wt%) indicating significant gel rigidity. In addition, they quickly recover to the original viscoelastic state after cessation of shear. The primary structure of the peptides can be designed to specifically control final gel properties. The turn sequence of the hairpin molecules is found to have drastic effect on the gelation kinetics and final rigidity. The hydrogels can also be reversible with pH or temperature. As the pH of the gel is lowered molecules unfold and the viscosity of the gel drops dramatically. It is also found that with the correct design of the molecules and solution conditions sol-gel transition temperatures can be tuned. At low temperatures the solutions showed liquid-like behavior while at transition temperatures (30 °C - 50 °C) the system forms a rigid hydrogel.

H3.14
Self-Assembling Physical Polymer Matrices Based on Affinity Interactions Between Peptides and Polysaccharides. Brandon Seal and Alyssa Panitch; Harrington Department of Bioengineering, Arizona State University, Tempe, Arizona.

Self-assembling polymers with affinity-based controlled release properties were developed based upon interactions between heparin-binding peptides and heparin. This hydrogel-like system mimics an extracellular matrix environment and also can sequester growth factors, peptides and drugs with affinity for sulfated polysaccharides. These therapeutics then can be released at rates dependent on heparin affinity. A heparin-binding peptide (PBD1) derived from the heparin-binding domain of antithrombin III was synthesized and conjugated to 4-arm poly(ethylene glycol) tetravinyl sulfone (PEG; 10,000 g/mol) such that four PBD1 molecules were bound to each PEG molecule. Heparin ($\sim$18,000 g/mol) was added to PEG-PBD1 ($\sim$18,000 g/mol) in a 1:3 molar ratio to create 10% (w/v) compositions in PBS, pH 7.4. Upon the addition of heparin, gel-like materials formed immediately and became homogenous following mixing. Dynamic mechanical testing at 25°C revealed a viscoelastic profile similar to that of concentrated, large molecular weight polymer solutions and melts. The PEG-PBD1 and heparin mixtures had gel-like properties between 25 and 100 rad/s with storage moduli ranging from 800 to 1650 Pa. In addition, the mixtures recovered quickly following thermal denaturation and mechanical insult. When added at a 2:1 molar excess compared with heparin, exogenous fluorescently-labeled peptides with varying affinities to heparin were successfully sequestered within the biopolymer matrices and subsequently released over several days at rates dependent on relative heparin affinity. The initial release rates ranged from 80% per day for a peptide with low heparin affinity to 0.6% per day for a peptide with strong heparin affinity. By altering the affinity of peptides to heparin, a series of peptides can be developed to yield a range of release profiles useful for controlled in vivo delivery of therapeutics. Due to the physical nature of the bonds within this system, these gel-like materials are conducive to in situ assembly and to direct application, via spreading, onto a tissue or surface of interest.

H3.15
Self-Assembling Protein Hydrogels via Engineered Coiled-Coil Domain Aggregation. Lixin Mi, Brian Chung, Stephen Fischer and James L Harden; Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

Coiled coils have been one of the major structural motifs studied in de novo protein design. In particular, many previous studies have used coiled coils as a molecular recognition motif for the self-assembly of inter- and intra-molecular structures, such as helix bundles. We have utilized such coiled coil design strategies to develop multi-block proteins that self-assemble into hydrogels with tailored microstructure and topology. These fibrilar, telechelic designs consist of a hydrophilic random coil (denoted R) flanked by associating coiled-coil end domains (denoted A, B, C). In this presentation, we will discuss a series of proteins with complimentary associating end blocks that preferentially form heterotrimer aggregates of A, B, and C domains. Both diblock structures (AR, BR, and CR) and triblock structures (XRY with X,Y=A, B, or C) have been studied. Circular dichroism measurments indicate that the helical and random coil blocks of these designs are structurally independent, and that the helical content and stability of the coiled-coil domains may be controlled by solution conditions such as pH and ionic strength. Size exclusion chromatography and analytical ultracentrifugation studies also reveal that equimolar mixtures of AR, BR, and CR proteins preferentially form heterotrimers in dilute solution. Analogous mixtures of symmetric triblocks ARA, BRB, and CRC in more concentrated solutions self assemble into viscoelastic network structures, which we have characterized using dynamic light scattering techniques. Such

hydrogels have wide potential applications in tissue engineering and drug control delivery, which are currently being developed.

H3.16
SNPs assay of nonlabeled leptin DNA based on biofunctional-modified surface. HeaYeon Lee and Tomoji Kawai; Osaka university, Osaka, Japan.

Numerous electrochemical sensors have been developed for use in the medical and biotechnology industries. The development of electrochemical biosensors has been significantly advanced by our knowledge gained in electron transfer processes. In the area of medical diagnostics, DNA biosensor protocols should allow for the rapid, sensitive and precise determination of DNA hybridization. Furthermore, it is also highly desirable to construct these DNA biosensors in an array to achieve a high throughput. We have developed a new electrochemical DNA chip protocol for the detection of unlabeled leptin DNA. Using an microarray consisting of biofunctional-modified gold electrodes, probe leptin oligonucleotides were attached through the application of a direct electric field. Electrochemical response changes originating from the hybridization of nucleic acids to protein-bound nucleic acids using soluble mediators in K4Fe(CN)6 solution could then be observed. The electrochemical protocol developed showed high sensitivity and good reproducibility in the detection of DNA hybridization. Significant changes in electrochemical signals were also observed when using target DNA with a single base mismatch, indicating the applicability of this method to SNPs (single nucleotide polymerase) detection. Recently we are extending this work to multi-channel electrochemical DNA chip microarray to reduce its size. And I will present SPM image of leptin DNA chip based on biofunctional-modified surface. The research has significant implication for the application of DNA in electronic devices and DNA-based electrochemical biosensors.

H3.17
Abstract Withdrawn

H3.18
Molecular Assembling Amphiphilic Peptide on Membrane-Associated Nano-Magnetite Particles for Protein Display. Tsuyoshi Tanaka and Tadashi Matsunaga; Tokyo University of Agriculture & Technology, Koganei, Japan.

Magnetospirillum magneticum AMB-1 synthesizes intracellular magnetite particles covered with lipid membranes. The membrane-associated magnetite particles (bacterial magnetic particle: BMP) have been used as magnetic carriers in immunoassay and DNA detection by conjugation of antibody and DNA. Until now, in vitro integrations have been successfully achieved using membrane protein-luciferase complexes, obtained from recombinant Escherichia coli. Recently, we have developed a novel technique for assembling hybrid proteins on BMP membrane using an amphiphilic peptide. An efficient insertion of amphiphilic peptides into membrane-associated magnetite particles is presented here as novel molecular anchors. Temporin L (13 amino acids), which is an antimicrobial peptide against gram-negative and gram-positive bacteria, was used as a model peptide. The peptide was assumed to form alpha-helical propensity. A modified Temporin L (Temporin L-A2), in which alanine was substituted in positions 3 and 7 from the N-terminus to reduce cationic content and form an overall alpha-helical propensity, was synthesized. Ribotoxin loop L3 (L3) and arginine-rich (R12), which are membrane-permeable carrier peptides to eukaryotic membrane, were synthesized as controls. The N-terminus of the peptides was labeled with a fluorescent dye, 4-fluoro-7-nitrobenzofurazan (NBD). Each peptide was added in 10 mM HEPES buffer containing BMPs, and incubated for 1 h with pulsed sonication. The effect of the insertion of NBD-peptide into BMP membrane was investigated by measuring the fluorescence of BMPs. The BMPs associated with Temporin L showed the highest fluorescence as compared with the derivate and controls. Therefore, the peptides were expected to insert into BMPs via an electrostatic interaction and hydrophobic interaction. Furthermore, the orientation of the peptide on BMPs was also investigated.

H3.19
Controlled Assembly of Dendrimer-like DNA. Yougen Li[1], Yolanda Tseng[1], Sang Kwon[1], J. Scott Bunch[2], Paul L. McEuen[2] and Dan Luo[1]; [1]Biological and Environmental Engineering, Cornell University, Ithaca, New York; [2]Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York.

DNA molecules possess many desirable chemical and physical properties as a polymeric material besides their genetic properties as inheritance information carriers. Furthermore, many tools have been available to manipulate DNA molecules (enzymes from molecular biology, for example). Therefore, great promise has existed for using DNA as a generic instead of a genetic material. Although much progress has been made in DNA computing and DNA nanotechnology recently, the full potential of DNA-based materials has not been achieved. This is in part duet to the fact that almost all DNA molecules, natural or synthesized, are either in linear or circular forms, which severely restrict their usefulness in molecular design and constructions. We have created branched Y-shaped DNA (Y-DNA) as novel building blocks and assembled, for the first time and in a controlled fashion, highly branched, tree-shape DNA dendrimers (termed "dendrimer-like DNA", or DL-DNA in short) from Y-DNA. The yield and the purity of higher generation DL-DNA did not seem to decrease even in the absence of purification, suggesting that the synthesis of Y-DNA and controlled assembly of DL-DNA were robust and efficient. The resulting DL-DNA molecules were stable and almost monodisperse. We also examined the 4th generation DL-DNA by atomic force microscopy (AFM) with both a standard tip and a single walled carbon nanotube (SWNT) tip, which revealed DL-DNA's highly branched dendritic nanostructure. TEM images also confirmed the nanoscale dendritic structure of DL-DNA. These DNA nanostructures are water-soluble, biocompatible and easy to synthesize. In addition, multivalent DNA dendrimers can be either isotropic or anisotropic, providing the possibility for conjugating other chemical entities including proteins and inorganic particles. Furthermore, the strategies and assembly approaches presented here can be easily employed to construct other non-linear, non-circular DNA building blocks that can be incorporated into even more complicated nanostructured material, thus providing great potential for applications in nanotechnology as well as in the rational design of novel, hybrid, nucleic acid-based nanomaterials.

H3.20
Micropatterning of Functional Lipid Domains for Toxin Detection. Jose Manuel Moran-Mirabal[1], Reid Nelson Orth[2], Dan Throckmorton[3], Anup K. Singh[3] and Harold G. Craighead[1]; [1]Applied and Engineering Physics, Cornell University, Ithaca, New York; [2]Biomedical Engineering, Cornell University, Ithaca, New York; [3]Microfluidics, Sandia National Laboratories, Livermore, California.

We have developed a method for patterning receptor-populated lipid domains at the micrometer scale. The receptors contained in these domains are functional and can bind toxin fragments, thus serving as biosensors. To pattern the lipid domains we have made use of a novel micro-patterning technique, which involves the etching of a polymer coating to expose specific areas of a silicon substrate (Ilic and Craighead, 2000.) The chip is then incubated with lipid vesicles, which fuse down on the silicon surface and form lipid bilayers as described by Orth et al. (2003.) Polymer lift-off following lipid deposition, reveals lipid patterns on the exposed areas of the silicon chip. The lipid domains range in size from 1-50 μm squares and rectangles. Toxin binding has been detected by epifluorescence down to 1 nM concentration making this a suitable technique for the detection of pathogenic proteins below infectious levels. Microfluidic network integration allows for preparation of independent lipid domains with different receptors to achieve simultaneous detection of several toxins in one chip.

H3.21
Pathological Self-assembly in Cystic Fibrosis Mucus. Lori K. Sanders[1], Thomas E. Angelini[2], Scott C. Slimmer[1] and Gerard C.L. Wong[1,2,3]; [1]Materials Science & Engineering, University of Illinois, Urbana, Illinois; [2]Physics, University of Illinois, Urbana, Illinois; [3]Bioengineering, University of Illinois, Urbana, Illinois.

Cystic Fibrosis (CF) mucus is a complex fluid consisting of mucin (a glycoprotein), lysozyme (a cationic antibacterial polypeptide), water, salt, as well as a high concentration of a number of anionic biological polyelectrolytes such as DNA and F-actin. The interactions governing these components are poorly understood, but may have important clinical consequences. For example, electrostatic self-assembly of these components into complex gels contributes significantly to respiratory distress, as well as to antibiotic sequestration, which leads to long-term infections. In this work, we investigate the structure of sputum collected from CF patients, as well as simulated model systems in vitro, using synchrotron small angle x-ray scattering. Preliminary results indicate the formation of lysozyme-actin complexes, and an unusual dependence of such self-assembly on KCl concentration and actin filament length. This work was supported by NSF DMR-0071761, the Beckman Young Investigator Program, and the Cystic Fibrosis Foundation.

H3.22
Spatial organization of fluorescent dye molecules using biopolymer-lipid self-assembly. lihua yang, Hongjun Liang and Gerard C. L. Wong; Materials Science and Engineering, Univ of Illinois at Urbana-Champaign, Urbana, Illinois.

Oppositely-charged lipid and biopolymers can self-assemble into a polymorphism of phases, due to entropically-controlled electrostatic

interactions. For example, cationic lipid and anionic DNA can spontaneous organize into a multilamellar structure with a 1-dimentional lattice of parallel DNA chains confined between 2-dimentional lipid sheets. The inter-DNA spacing can be reversibly tunable between 2.5 nm and 6 nm, which essentially defines a nanoporous complex with a tunable pore size. These nanoporous DNA-membrane complexes have been recently used to organize metal ions for CdS templating. In this work, we use biopolymer-lipid complexes to organize charged fluorescent dye molecules, in order to generate nanoscopic coupled arrays with novel optical properties. A number of biopolymers of different charge densities, diameters and persistent lengths have been employed to optimize the self-assembly. Preliminary results will be presented.

H3.23
Bio-Organic Nanotechnology: Using Proteins and Synthetic Polymers for Nanoscale Devices. Linda K. Molnar[1,2], Ting Xu[3], Thomas P Russell[3] and Jonathan D Trent[1,2]; [1]Astrobiology Technology Branch, NASA Ames Reseach Center, Moffett Field, California; [2]Center for Nanotechnology, NASA Ames Reseach Center, Moffett Field, California; [3]Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts.

While the ability of proteins to self-assemble has made them a powerful tool in nanotechnology, in biological systems protein-based structures ultimately depend on the context in which they form. We combine the self-assembling properties of synthetic diblock copolymers and proteins to construct intricately ordered, three-dimensional polymer/protein structures with the ultimate goal of forming nano-scale devices. This hybrid approach takes advantage of the capabilities of organic polymer chemistry to build ordered structures and the capabilities of genetic engineering to create proteins that are selective for inorganic or organic substrates. Here, microphase-separated block copolymers coupled with genetically engineered heat shock proteins are used to produce nano-scale patterning that maximizes the potential for both increased structural complexity and integrity.

H3.24
Abstract Withdrawn

H3.25
Nanoparticles Capped with Thiol-Containing Amino Acids. Elizabeth Crew, Li Han, Nancy Kariuki, Christopher Trinidad, Jin Luo and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

We have recently been investigating the interactions and reactivities of thiol-containing amino acids with metal nanoparticles. This investigation is important for exploring potential applications of metal nanoparticles as advanced materials in biomedical fields. For example, rapid and reproducible assays of plasma levels of homocysteine are essential for understanding its pathogenic role. This presentation describes recent findings of an investigation of the unique interfacial reactivity and optical properties of gold and alloy nanoparticles capped with various thiol-containing amino acids. The interfacial reactivity of gold nanoparticles in the presence of a variety of sulfur-containing amino acids has been systematically investigated. The relative concentration and chain length of thiol-containing amino acids have been found to affect the size and interparticle spatial properties of the nanoparticles. Implications of the findings to the development of biomedical materials for screening of thiol- or sulfide-containing amino acids will also be discussed.

H3.26
Effect of Sol-Gel Encapsulation on Enzyme Structure and Function: A Small Angle Neutron Scattering Study. Lisa E. Rodgers[3,2], Peter J. Holden[2], L. John R. Foster[3], Robert B. Knott[4], Kim S. Finnie[1] and John Bartlett[1]; [1]Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia; [2]Environment, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia; [3]School of Biotechnology and Biomolecular Sciences, University of NSW, Sydney, New South Wales, Australia; [4]Bragg Institute, Australian Nuclear Science and Technology Organisation, Menai, New South Wales, Australia.

Sol-Gel technology provides a facile, intrinsically low temperature approach to the immobilisation of either inorganic or organic species and has recently been extended to include immobilisation of active biological cells or proteins primarily for biosensor applications. Application to biocatalysis is in its infancy and the key to success lies in the characterisation of the relationship between gel structure, maintenance of active state of the proteins and cells and optimisation of catalytic activity. The application of small angle neutron scattering (SANS) to characterisation of sol-gel based bioencapsulates offers the opportunity to examine this relationship. Enzymes such as Candida antarctica lipase B (CALB) have been found to have dramatically increased activities when immobilised in sol-gel hosts and are applied in a variety of industrial processes, making them suitable candidates for SANS structure/activity studies. Contrast variation studies enable the structures of the bioencapsulates and the sol-gel host to be explored independently, giving information about the interaction between them and the role of the inorganic/biological interface in mediating bioactivity. Characterising both the solution state and the immobilised form of an enzyme, as well as their respective activities, enables both the conformational and biocatalytic effects of sol-gel encapsulation to be assessed. We report here the determination of the activities of the free and encapsulated forms of CALB and its conformation in dilute solution. Gels were produced by fluoride-catalysed hydrolysis of mixtures of tetramethylorthosilicate (TMOS) and methyltrimethoxysilane (MTMS). Phase separation between the enzyme and the evolving sol-gel matrix was minimised by incorporating glycerol into the sol-gel precursor solution. Incorporation of glycerol appeared to enhance the stability and bioactivity of the encapsulated enzyme. The potential effect of the sodium fluoride catalyst upon the enzyme was also investigated. The deduction of structure/property correlations and a rigorous understanding of the effects of sol-gel encapsulation upon biological entities are being developed. The application of neutron scattering techniques and activity studies to elucidating the effects of sol-gel bioencapsulation on structure and bioactivity will be discussed.

H3.27
Novel Method for the Investigation of the Morphologies of biological Self-Assembled Monolayers. Arum A Yu[1], Julie Norville[2], Marc Baldo[2], Barry D Bruce[3] and Francesco Stellacci[1]; [1]Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]RLE, Department of Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts; [3]Department of Biochemistry and Cellular and Molecular Biology, University of Tennessee, Knoxville, Tennessee.

Recently there has been a large effort in developing advanced biological sensors. Many of these sensors (e.g. micro gravimetric balances or surface plasmon resonance bio-sensors) are based on self-assembled monolayers of biological molecules such as proteins or protein receptors. The role of the molecules bound to the surface is to react with other bio molecules (such as proteins) present in solution and attract or bind them to the surface. This produces a change in the environment that is detected as signal. In order to maximize such effect it is desirable to control the morphology of the protein on the surface so to, for example, have all of the receptor groups pointing out toward the solution. Unfortunately, there is not an efficient method for probing the conformation of a monolayer of proteins or complex bio-SAMs on surfaces. We introduce here a new method for imaging proteins based on electrostatic driven phase imaging in tapping mode Atomic Force Microscopy (AFM). The method is relies on the detection of differences in AFM phase images obtained when applying various voltages on the AFM tip. It is known that phase images of organic materials depend on the dissipative component of the mechanic response of the probed sample (i.e. its viscoelastic properties). The applied electric field activates new dissipative channels just in the polar parts of the sample. Consequently it is possible to distinguish polar from apolar parts in a monolayer. A quantitative analysis of the phase shift as a function of the polarity of the monolayer will be discussed. Results that help understand the conformation of a monolayer composed of a photosynthetic protein will be presented, it will be shown that via this method it is possible to make conclusion about the conformation of the protein assemble on the gold surface.

H3.28
DNA Adsorption to Peptide Liposomes via Hydrogen Bonding Interactions. Bruno F Marques, Nicole M Gartner and James W Schneider; Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Cationic liposomes are one of the most promising types of nonviral gene delivery vectors. However, their ionic-strength-dependent DNA-binding properties have been shown, in some cases, to cause vesicle reorganization and loss of surface bioactivity. We will show here that peptide liposomes can overcome these effects by binding DNA via hydrogen bonding interactions. The peptide utilized in our systems is peptide nucleic acid (PNA), a synthetic mimic of DNA that replaces the negatively charged sugar-phosphate backbone with a charge-neutral, highly flexible peptide backbone. PNA has been shown to bind to complementary nucleic acid sequences with higher affinity and specificity than traditional oligonucleotides. By using short (1∼3 bases), heterogeneous sequences of PNA on the surface of liposomes, we are able to nonspecifically target multiple short regions of the DNA strand, thus protecting bound DNA against the action of nucleases. Furthermore, DNA binds in a sequence-specific manner to longer (6∼10 bases) PNA sequences. Using UV measurements and size

exclusion chromatography, we have quantified the extent of PNA incorporation in the liposomes, as well as the extent of DNA binding under various conditions. Through those measurements, we found that DNA binding occurs with 90% efficiency up to a critical amount of PNA, after which liposomes undergo morphological changes. This critical surface concentration varies for different PNA molecules depending on the headgroup area, phase behavior, and surface arrangement of each molecule. To determine how each of these variables affects vesicle reorganization during DNA binding, we have been using Langmuir-Blodgett monolayers and fluorescence microscopy, which allow us to analyze the surface arrangement of the peptides at various stages of the binding process. Maintaining vesicle morphology upon DNA binding allows cell-surface receptors to retain their bioactivity, which is essential for biotechnology applications, such as gene therapy and biosensing. We will also discuss efforts to selectively bind and release DNA by taking advantage of phase through external stimuli (i.e. temperature, pH).

H3.29

Biological Muscle as Self Assembled Actuator. Vaclav Bouda[1], Lea Boudova[2] and Denisa Haluzikova[2]; [1]Faculty of Electrical Engineering, Czech Technical University, Prague, Czech Republic; [2]Institute of Sport Medicine, Charles University, Prague, Czech Republic.

Skeletal muscles are built of micro-sized contractile units called sarcomeres, which contain two filaments types: thin and thick. Thin (actin) and thick (myosin) protein filaments together with the myosin heads attached to the myosin filaments are recognized to play a central role in contraction. Swinging of the myosin heads drives the thin filaments toward the center of the sarcomere, thereby shortening both the sarcomere and the muscle. One of our most interestring results is that the myosin heads have a multiplex function. The myosin heads seem to be predominant elements that control the evolution of the internal structure of the sarcomere. The presentation describes the effects of both van der Waals forces and electrostatic repulsive forces on the self-organization of internal structure of the sarcomere. In the state of sarcomere relaxation, there is a secondary minimum in the interaction energy determining the equilibrium distance between the myosin heads. The sarcomere contraction is interpreted as calcium induced rearrangement and swing of myosin heads, which result in relative actin-myosin sliding. Application of the process can provide the engineer and physicist with a simple analogy to nano-actuators of highest performance.

H3.30

Macromolecule-Crystal Binding in Calcium Oxalate Biomineralization. Xiaoxia Sheng[1], Jeffrey A. Wesson[2] and Michael D. Ward[1]; [1]Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota; [2]Medical College of Wisconsin, Milwaukee, Wisconsin.

Kidney stones are crystal aggregates, most commonly containing calcium oxalate monohydrate (COM) crystals as the primary constituent. In vitro studies have suggested that anionic molecules or macromolecules with substantial anionic functionality (e.g., carboxylate) play an important role in the crystal growth of calcium oxalate, its aggregation, and the attachment of these crystals to renal epithelial cells. We describe here atomic force microscopy (AFM) studies that examine the influence of the polymeric additives on the crystal growth and directly measure the adhesion between molecules and COM crystal faces. Face-selective binding of each polymer and its impact on the growth of different crystal faces were deduced by in situ dynamic AFM imaging in the presence of the polymeric additives, including synthetic macromolecules (poly aspartic acid (polyD) and poly glumatic acid (polyE)) and native protein (osteopontin (OPN)). PolyD exerts greater influence on growth in the <001> direction, while OPN and polyE suppress the growth along the <010> direction. The concentration dependence indicates PolyE has an overall weaker effect on the growth rates than polyD, which has weaker effect than OPN. The measurement of adhesion forces between tip-immobilized molecules and the COM (100) surface in aqueous media supports an important role for the carboxylate group in processes responsible for kidney stone formation, specifically macromolecule-mediated adhesion of COM crystals to cells and crystal aggregation. The comparison of the adhesion forces for COM (100) and COM (010) directly proved the preferred binding of carboxylates on COM (010). The presence of polyD or polyE during force measurements results in a reduction in the adhesion force measured for carboxylate-modified tips, consistent with blocking of binding sites on the COM (100) surface by the carboxylate-rich polymer. Several native proteins were examined to describe their ability on mediating the adhesion force between carboxylates and CaOx crystal surfaces. These microscopic events observed by AFM reveal some of the critical phenomena associated with protein-crystal interactions responsible for regulating the physiological behavior of calcium oxalate biominerals.

H3.31

How Organic Monolayers Control the Shape of Growing Minerals. Dorothy M. Duffy and John H. Harding; Physics and Astronomy, University College London, London, United Kingdom.

Living organisms can control the size, shape and structure of minerals. Attempts to reproduce this biological control in the laboratory often use Langmuir monolayers of long-chain carboxylic acids. We use a combination of large-scale molecular dynamics simulations and the Wulff-Kaishew theorem to predict the morphologies of calcite crystals grown on stearic (octadecanoic) acid monolayers and find good agreement with experiments. To achieve this, it is essential to go beyond models of the monolayer as a substrate providing a pattern that the growing crystal must fit. Organic monolayers are not rigid structures in a vacuum. They are flexible, chemically active surfaces in contact with water. Our simulations demonstrate that the nucleation of calcite crystals on organic substrates is controlled by competition between the interactions of the crystal and water with the substrate. Fully ionised substrates have stronger adhesion to the crystal surfaces than neutral substrates and are therefore better at promoting nucleation. The pH of the solution both promotes nucleation and controls crystal shape since the ionised and neutral monolayers stabilise different surfaces, (10.4) for the neutral case, (10.0) or (00.1) for the ionised case. The density of the surface ions also constrains the nucleation of surfaces on ionised substrates. This must be low enough to permit the substitution of each ion by charge groups of the substrate to create a neutral interface. The commonly observed (01.2) interface has a reduced density of calcium ions at the interface to satisfy this constraint. Detailed stereo-chemical matching is of minor importance; the flexibility of the template ensures that many different patterns can be fitted to a given template. The competition with water molecules already present, the state of ionisation of the monolayer and the density of surface carbonate ions are much more important.

H3.32

Molecular Modulation of Calcium Oxalate Crystallization by Osteopontin and Citrate. Roger Qiu[1], Andrzej Wierzbicki[2], Christine A Orme[1], Anita M Cody[3], John R Hoyer[4], George H Nancollas[5], Salvador Zepeda[6,1] and James J De Yoreo[1]; [1]Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Chemistry, University of South Alabama, Mobile, Alabama; [3]Department of Geological and Atmospheric Sciences, Iowa State University, Ames, Iowa; [4]The Children's Hospital of Philadelphia, University of Pennsylvania, Philadelphia, Pennsylvania; [5]Chemistry Department, University at Buffalo, State University of New York, Amherst, New York; [6]Department of Chemical Engineering and Materials Science, University of California, Davis, Davis, California.

Understanding molecular mechanisms of biological control over calcium oxalate crystallization is crucial for development of effective stone disease therapies. Moreover, extension to other systems may suggest strategies for synthesis of biologically inspired materials. Calcium oxalate monohydrate (COM), which plays a functional role in plant physiology, is a source of pathogenesis in humans, causing kidney and renal stone disease. Despite extensive research on COM modification by proteins and small molecules, the control mechanisms remain unknown. In addition, because proteins directing COM inhibition have been identified and sequenced, it provides a realistic system for general physiochemical investigations of biomineralization. Here we report the first molecular-scale picture of COM modulation by both osteopontin - a naturally occurring protein- and citrate - a commonly used therapeutic agent. Combining force microscopy with molecular modeling, we show that each controls growth habit and kinetics by pinning step motion on different faces through specific interactions where both size and structure determine the effectiveness. Moreover, the results suggest synergistic effects of simultaneous action by both modifiers. This work demonstrates the utility of combining molecular imaging and modeling tools to understand events underlying aberrant crystallization in disease. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48, and was supported in part by grants DK61673 and DK33501 from the National Institutes of Health.

H3.33

Electrostatic and Hydrodynamic Fields Influence *InVitro* Polycationic Peptide-Mediated Silica Biomineralization. Francisco Rodriguez[1,2], Diana D. Glawe[3], Rajesh R. Naik[1,4], Kevin P. Hallinan[2] and Morley O. Stone[1]; [1]Materials Directorate, Air Force Research Laboratories, Wright-Patterson AFB, Ohio; [2]Department of Mechanical and Aerospace Engineering, University of Dayton, Dayton, Ohio; [3]Department of Engineering Science, Trinity University, San Antonio, Texas; [4]Materials Directorate, UES, Inc., Dayton, Ohio.

The ability to physically influence polycationic peptide-mediated silica

biomineralization morphologies resulting in a series of complex 2-D and 3-D silica networks is demonstrated. Overall silica morphologies are shown to differ from the sphere-like dispersed particles normally obtained *invitro*. Two forms of external force fields were imposed on the biomineralization process, namely: electrostatic and hydrodynamic fields. These findings suggest that the future development of bio-inspired complex 2-D and 3-D silica based micro/nano-composite materials is possible. For example, silica-based micro/nano-composite materials formed using precisely controlled external force fields could lead to the directed deposition of silica, where size and morphologies are controlled *insitu*, resulting in materials with unique mechanical, electrical, magnetic, and optical properties.

H3.34

Heterogeneous Nucleation of Calcium Oxalate Dihydrate on Amorphous Calcium Phosphate: Implication to Kidney Stone Formation. Fairland Fontillas Amos[1], Sivakumar Munisamy[1], Saeed R Khan[2] and Laurie B Gower[1]; [1]Materials Science and Engineering, University of Florida, Gainesville, Florida; [2]Department of Pathology, University of Florida, Gainesville, Florida.

The role of calcium phosphate on the nucleation of calcium oxalate has been examined due to its importance in kidney stone formation. Most of the in-vitro studies in this area involve the formation of calcium oxalate (CaOx) on crystalline calcium phosphate, e.g. hydroxyapatite (HA) and brushite. In this study, an alternative route to the synthesis of CaOx-calcium phosphate composite is explored through nucleation of CaOx on amorphous calcium phosphate (ACP) spherical particles. ACP is prepared through polymer-induced liquid precursor (PILP) process.* Images from scanning electron microscopy reveal that the calcium oxalate grown on ACP in the presence of polyvinyl phosphonic acid and polyaspartic acid produce mushroom-shaped spherulites that are not seen in the homogeneous nucleation of calcium oxalate. The spherulites appear to have ACP-rich core with CaOx overgrowths. Data from x-ray diffractometry reveals that the CaOx is in the dihydrate form. This CaOx-ACP composite structure is consistent with the structure of typical urinary stones with the exception that kidney stones normally have HA core. However, we have seen that the ACP particles transform into HA over a period of time which likely occurs in the central core of these synthetic composites as well. This system might serve as a useful in vitro model for examining the complex mechanism in kidney stone formation. *Gower LB, Odom DJ. J CRYST GROWTH 210 (4): 719-734 MAR 2000.

H3.35

The Chemical Inhomogeneity of Fluid-Inclusions and Shell Calcite Matrix - A Combined Micro-Raman, Microthermometric and LA-ICP-MS Investigation. Erika Griesshaber[1], Reinhart Job[2], Thomas Pettke[3] and Alfons van den Kerkhof[4]; [1]Department of Geology, Mineralogy and Geophysics, University of Bochum, Bochum, Germany; [2]Department of Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany; [3]Institute of Isotope Geochemistry, ETH Zurich, Zurich, Switzerland; [4]Center for Geoscience, University of Gottingen, Gottingen, Germany.

In a combined micro-Raman, microthermometric and Laser-ICP-Mass-Spectrometric investigation the chemical inhomogeneity of shell calcite and fluid-inclusions incorporated within the calcite matrix has been analysed. For the assessment of vital effects and signatures of recrystallisation processes the measurements were performed on both, modern and fossil brachiopod shells derived from distinct marine environments. The here presented study should be regarded as an example for the possibility to analyse very small amounts of material with a spatial resolution of 3 to 8 μm. The combined application of these high-resolution analytical methods enables the investigation of current problems of bio material and biomineralisation science as well as of paleoceanography. A complementary EBSD and PIXE investigation of the microstructure of the shells is given by Schmahl et al. (1). Micro-Raman analyses show that the shells are penetrated from both margins along punctae by sea-water. LA-ICP-MS analyses along outer - inner transects of the shell matrix reveal distinct chemical inhomogeneities, especially within the valve region. Traces of ambient seawater seems to be preserved in fluid-inclusions of both, modern and fossil samples. Microthermometric analyses indicate that most inclusions are filled with a highly concentrated NaCl solution, about twice as much NaCl concentration than modern seawater, although NaCl solutions in fluid-inclusions along the mantle margin are less concentrated than at the sea ward margin. Thus a finger-print of ambient sea-water is preserved within these shells. (1) W. Schmahl, E. Griesshaber, C. Korte, R. Job, R. Neusser and J. Meijer (2003): The formation of brachiopod shell calcite - a combined texture and chemical analysis. Abstract submitted to the MRS Fall Meeting, Boston 2003.

H3.36

The Microstructure Of Brachiopod Shell Calcite - A Combined Texture And Chemical Investigation. Wolfgang W. Schmahl[1], Erika Griesshaber[1], Christoph Korte[1], Reinhart Job[2], Jan Meijer[3] and Rolf Neuser[1]; [1]Department of Geology, Mineralogy and Geophysics, University of Bochum, Bochum, Germany; [2]Department of Electrical Engineering and Information Technology, University of Hagen, Hagen, Germany; [3]Department of Physics, University of Bochum, Bochum, Germany.

The architecture of inorganic bio-materials is of interest as prototypes for the design of optimized materials. Furthermore, an understanding of biomineralisation - the biologic control of crystal growth - may lead to new fabrication techniques. Apart form the work on molluscs by Chateigner et al. (1), which concentrated on aragonitic shells, the here presented investigations are the first crystallographic microstructure analyses on brachiopod shell calcite. We have investigated microstructural characteristics of the shell structure of the modern brachiopod Megerlia truncata by SEM and EBSD. The inorganic component of the secondary layer (Samtleben et al. 2001) consits of fibrous calcite single crystals. They show both, a shape and a crystallographic preferred orientation. The morphological fibres are 5 to 10 microns wide and up to 100 microns long, possibly even longer. The fibres are stacked in parallel to complex-shaped blocks of about 100 microns diameter, and the direction of the fibre axis changes from block to block, frequently into perpendicular direction, presumably enhancing the strength of the structure. Although the crystal fibres are curved, the orientation of the crystallographic axes is constant along a single fibre, while it changes between neighboring fibres. Locally, the crystallographic texture is a strong [001]hex axial-texture with no preferred orientation of the <100>hex directions. The [001]hex directions of the crystallites point perpendicular to the outer walls of the shell. The morphological fibre axis, however, is parallel to the shell wall, and its crystallographic direction is arbitrary in the plane perpendicular to [001]hex. Complementary cathodoluminescence and high space-resolution PIXE analyses show large chemical inhomogeneities between the primary and the secondary shell layer as well as within the hinge region. While Sr, Mn and Fe concentrations decrease from the outward margin towards the mantle margin Ca concentrations increase complementarily. (1) Chateigner D., Hedegaard C. and Wenk H.-R. (2000): Mollusc shell microstructures and crystallographic textures. J.Struct.Geol., 22, 1723-1735. (2) Samtleben C., Munnecke A., Bickert T. and Patzold J. (2001): Shell succession assemblage and species dependent effects on the C/O-isotopic composition of brachiopods - examples from the Silurian of Gotland. Chem. Geol., 175, 61-107.

H3.37

Selective Control of Mineral Polymorph during Thin Film Deposition via a Polymer-Induced Liquid-Precursor (PILP) Process. Lijun Dai, Munisamy Sivakumar and Laurie B Gower; Materials Science and Engineering, University of Florida, Gainesville, Florida.

Calcium carbonate-polymer composites have been of recent interest by the biomimetics community because of the outstanding mechanical properties of mollusk nacre. Advancements have been made towards making mineral thin-films, which can conceivably be used in a sequential deposition to create multi-layered organic-inorganic composites. However, there has been a lack of control of the polymorph of the mineral film in these synthetic composites. This aspect could be important for regulating both the morphology and mechanical properties of the mineral phase, as is the case in biominerals, which have a high degree of control over crystal polymorph. Here, we have used crosslinked polyvinyl alcohol (PVA) films as substrates to study the crystallization of calcium carbonate films formed by the addition of acidic polymer, which is used to induce the polymer-induced liquid-precursor (PILP) process [Gower & Odom, 2000]. In the first system, vapor diffusion of ammonium carbonate was used to raise the supersaturation of a calcium chloride crystallizing solution. In the second system, dropwise addition of calcium chloride or ammonium carbonate into each other was used to raise supersaturation. We systematically examined the following factors with respect to their influence on polymorphs of $CaCO_3$ thin films deposited on PVA subsrates: supersaturation degree and stoichiometric ratio of $Ca^{2+}/CO_3{}^{2-}$; Mg-ion impurity, concentration and location of acidic polymer (polyaspartic or polyacrylic acid); vapor diffusion time; and time of substrate introduction. By carefully adjusting these factors, we were able to selectively synthesize this films of calcite, vaterite, aragonite, and monohydrocalcite. A discussion of the mechanisms governing the polymorphic selectivity will be presented. Gower, L. B. & Odom, D. J. Deposition of calcium carbonate films by a polymer-induced liquid-precursor (PILP) process. J. Crystal Growth 210:4, 719-734 (2000).

H3.38

Biomimetic Mineralization of Collagen with Calcium

Phosphate by a Polymer-Induced Liquid-Precursor (PILP) Process. Munisamy Sivakumar, Matt J Olszta and Laurie B Gower; Materials Science and Engineering, University of Florida, Gainesville, Florida.

The mineralization of collagen in vitro is of great interest for understanding the mechanisms underlying the mineralization of bone in vivo, as well as for the biomimetic fabrication of synthetic bone graft substitutes. Natural biocomposites such as bone exhibit a nanostructured architecture of hydroxyapatite crystals well arranged within the collagen fibrils, to form a unique interpenetrating composite. In this study, in situ mineralization of collagen with hydroxyapatite was carried out under simulated physiological conditions using acidic macromolecules, such as poly(aspartic acid) and poly(vinyl phosphonic acid), to induce an amorphous liquid-phase mineral precursor. The novelty of our approach is that the polymer-induced liquid-precursor (PILP) phase can be drawn by capillary action into the gaps and grooves of the collagen matrix. The PILP phase then subsequently crystallizes into hydroxyapatite as the waters of hydration are thermodynamically driven off, leaving the collagen embedded with nanocrystals, and generating a highly mineralized composite that mimics the nanostructured architecture of bone, as revealed by FT-IR spectroscopy, X-ray diffraction and electron diffraction. Etching studies reveal that the mineral phase is generated both on and within the collagen fibrils, leading to an interpenetrating network of mineral and collagen. We hypothesize that this in vitro model system is simulating the intrafibrillar mineralization of collagen that occurs in secondary bone formation, and offers a promising approach for the development of new hard-tissue implant materials such as bone and teeth.

H3.39
Biomimetic synthesis of novel composite materials. Suresh Valiyaveettil, Chemistry, National University of Singapore, Singapore, Singapore.

Hard material synthesis in Nature is beleived to be controlled by biomacromolecules such as protiens and play an important role towards the survival of the species. Recent advances in biomineralization process is beginning to show some light on this fascinating process of bulk material synthesis. Often, the observed morphologies and the control exerted by the biomacromolecules on the structure and properties of these materials are difficult to reproduce in the laboratory conditions. We have been interested in unlocking the molecular mechanism for the formation of highly structured architectures such as eggshells (JBC 2003, 278 (5), 2928-36; PNAS 2002, 99, 5155-59). This presentation will highlight our various approaches to understand this process and traslate that knowledge towards developing unique composite materials.

H3.40
Organic Template-Directed Hydroxyapatite Crystallization: Evaluation with IR External Reflection Spectroscopy. Kimiyasu Sato[1], Yuri Kumagai[2], Koji Watari[1] and Junzo Tanaka[3,2]; [1]Ceramic Research Institute, National Institute of Advanced Science and Technology, Nagoya, Japan; [2]CREST, Japan Science and Technology Corporation, Kawaguchi, Japan; [3]Biomaterials Center, National Institute for Materials Science, Tsukuba, Japan.

Organic template-directed crystallization of hydroxyapatite was studied in situ via Fourier transform IR external reflection spectroscopy. Langmuir monolayer of arachidic acid was formed on a surface of simulated body fluid, which possesses inorganic ion concentrations and a pH almost equal to those of human blood plasma. Owing to the chemical interactions between inorganic ions and carboxyl group, heterogeneous nucleation of hydroxyapatite occurred under the monolayer. The absorbances of the antisymmetric and symmetric methylene stretching bands increased during the crystallization process, which means that conformational change of hydrocarbon chain occurred. Interfacial interactions between organic templates and induced crystals are often discussed only through comparisons of two-dimensional spacing of organic headgroups with that of coplanar ion arrangements in the crystals. However, the present study implies that the Langmuir monolayer changes its structure to optimize the geometrical fit to the induced hydroxyapatite crystals.

H3.41
Molecular imprinting of biomineralized CdS nanostructures: Crystallographic control using self-assembled DNA-membrane templates. Hongjun Liang[1], Thomas E. Angelini[2], Paul V. Braun[1] and Gerard C.L. Wong[1,2,3]; [1]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; [2]Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois; [3]Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

A wide range of biomineralization and templating methods exist for organizing inorganic materials at a wide range of length-scales. Here, we show that crystallographic control of the inorganic nanostructures is possible using synthetic biomolecular templates comprised of anionic DNA and cationic membranes, which self-assemble into a multi-lamellar structure where a periodic one dimensional (1D) lattice of parallel DNA chains is confined between stacked two dimensional (2D) lipid sheets. We have organized Cd^{2+} ions within the interhelical pores between DNA strands, and subsequently reacted them with H_2S to form CdS nanorods of controllable widths and crystallographic orientation. The strong electrostatic interactions align the templated CdS (002) polar planes parallel to the negatively charged sugar-phosphate DNA backbone, which indicates that molecular details of the DNA molecule are imprinted onto the inorganic crystal structure. The resultant nanorods have (002) planes tilted by 60° with respect to the rod axis, in contrast to all known II-IV semiconductor nanorods.

H3.42
Laser Light Scattering Observations of a Polymer-Induced Liquid Precursor Process for Calcium Carbonate Mineralization. Elaine DiMasi[1], Matthew J. Olszta[2], Laurie B. Gower[2] and Tianbo Liu[1]; [1]Physics Department, Brookhaven National Laboratory, Upton, New York; [2]Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

The presence of biopolymers strongly affects mineralization from solution, through processes which are poorly understood but are important in biomineralization and biomimetic materials science. We have found that the presence of acidic polypeptides, such as poly(acrylic acid) or poly(aspartic acid), can drive mineralization of calcium carbonates through an amorphous precursor phase, in some cases with a stage of liquid-liquid phase separation that allows $CaCO_3$-rich droplets to form and subsequently crystallize. Here we present the first in-situ sub-micron observations of this polymer-induced liquid-precursor (PILP) process by laser light scattering. Static and dynamic light scattering data were obtained from $CaCl_2$ solutions containing poly(aspartic acid) and exposed to the decomposition products of ammonium carbonate. The measurements probe the average scatterer mass and apparent hydrodynamic radius $R(h, app)$ of the droplets as they nucleate and coalesce. The data reveal three stages of the PILP process: an early stage of droplet growth to $R(h, app) \approx 250$ nm; a mid-time stage of fluctuations and polydispersity in particle size; and a final growth period where $R(h, app)$ increases from 350 nm to the micron scale. We will discuss possible models of nucleation, aggregation, and dehydration that occur in the presence of the polymer.

H3.43
Equilibrium Hydration Structure and Protein Resistance. Manfred P. Heuberger, Tanja Drobek and Nicholas D. Spencer; Department of Materials, Swiss Federal Institut of Technology (ETH), Zuerich, Zuerich, Switzerland.

It is known that certain liquids bear finite compressive loads when confined between two surfaces at separations of a few molecular diameters. The commonly accepted interpretation of these observations invokes liquid structuring. Similar structural forces in water are found in conjunction with the phenomenon of hydration. In biological systems, the structure of water and the related hydration forces play a crucial role determining the specific bio-molecular functionality. The adsorption of proteins on surfaces is of high relevance for drug delivery and the design of bio-materials: Polyethylene glycol (PEG)-based surface grafts are known for their capability to render a surface resistant to non-specific protein adsorption. The steric repulsion that originates from the flexible PEG chains is commonly invoked as theoretical basis for this protein-resistance. Still, both PEG and proteins are highly hydrated structures. In fact, the extraordinarily water-solubility of PEG is commonly attributed to an exceptional structural fit between PEG and water. We present the first direct force measurements that indeed show the existence of such equilibrium hydration structures in hydrated PEG brushes. High-resolution measurements obtained with the extended surface forces apparatus reveal structural forces that are superimposed to the known steric repulsion. The fundamental relevance of these results for the phenomenon of protein-resistance is discussed.

SESSION H4
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Tuesday Morning, December 2, 2003
Back Bay B (Sheraton)

8:30 AM *H4.1
Antimicrobial Oligomers. William F. DeGrado, Department of

Biochemistry & Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania.

The design of polymers that mimic the complex structures and remarkable biological properties of natural proteins is an important endeavor. Recently, a number of non-natural peptides with designed sequences have been elaborated to provide biologically active structures; in particular, facially amphiphilic peptides built from beta-amino acids have been shown to mimic both the structures as well as the biological function of natural antimicrobial peptides such as magainins and cecropins. However, these natural peptides, as well as their beta-peptide analogues, are expensive to prepare and difficult to produce on a large scale, limiting their use in materials as well as pharmaceutical applications. We report herein on the design of a series of oligomers and polymers that capture the physical and biological properties of this class of antimicrobial peptides, but are easy to prepare from inexpensive monomers. This new class of amphiphilic polymers may find application in situations where inexpensive antimicrobial agents are required.

9:00 AM *H4.2
Lipidation of Antimicrobial Peptides Promotes Activity through Formation of Secondary Structure. Matthew Tirrell, Alexander Chu-Kung and Kristen Bozzelli; Chemical Engineering and Materials, University of California, Santa Barbara, California.

Antimicrobial peptides are ubiquitous natural antibiotics that are diverse in amino acid sequence. Despite their diversity, these peptides share several common features, including: a large net positive charge, a disordered structure in solution, and the potential for forming amphipathic structures under certain environmental conditions. Killing activity of these peptides has been linked to their ability to transition from random coil structures in solution to amphipathic secondary structures in the presence of cell membranes. We have previously shown that lipidation of peptides can increase the formation and stability of their secondary structure. We lipidated a series of three peptides and tested the effect on their structure, antibacterial activity, and eukaryotic cell toxicity. When lipidated, all of the peptides show increased antimicrobial activity as measured by MBC and/or ONPG assays. The CD spectra of the lipidated samples showed a corresponding increase in their α-helical content in a PG/PE-containing solution, which mimics bacterial membranes. In the presence of PC vesicles, which mimic the cell membrane of eukaryotic cells, two of these peptides showed little change in their structure upon lipidation. The corresponding hemolytic activity of these peptides remained low. One peptide showed a large increase in hemolytic activity upon lipidation and also showed a marked increase in helical content in the presence of PC vesicles. These results support the theory that activity of antimicrobial peptides, either hemolytic or antimicrobial, is linked to the change in secondary structure when introduced to lipid membranes. Lipidation of peptides may improve their usefulness as antimicrobial agents by enhancing their ability to form the necessary secondary structure to interact with target membranes.

9:30 AM *H4.3
Fabrication of Novel Biomimetic Polymers Using Combinatorial Peptide Screening Technologies.
Archit Bharat Sanghvi[1], Kiley P-H Miller[2], Angela M Belcher[2] and Christine E Schmidt[1]; [1]Biomedical Engineering, the University of Texas at Austin, Austin, Texas; [2]Bioengineering, Massachusetts Institute of Technology, Massachusetts, Massachusetts.

The rapid growth in the use of synthetic polymers in medicine and biotechnology has prompted the development of advanced biomaterials that display both biocompatible and bioactive properties. A large variety of biological functions could be programmed into materials including: ligands that bind cellular receptors, drugs for targeted delivery, and antibodies for detection or binding. In particular, we are interested in the surface modification of existing synthetic materials using combinatorial phage display technology to control cellular behavior and to direct tissue formation. Ideally, surface modification techniques should provide an inherent flexibility to permit changes in molecular design for a broad range of applications and should be straightforward to implement. There have been many techniques used to modify the surfaces of biomaterials including protein adsorption and self-assembly, synthesis of novel graft-copolymers with desired functional groups, and direct covalent surface modifications. To address the limitations of these approaches, we are designing a surface that precisely activates specific biological pathways using a new method for biomolecule immobilization. Specifically, we have used combinatorial phage display technologies to select for unique polymer-specific peptide sequences that have direct binding to the polymer's surface. We have used a commerically available genetically engineered, random bacteriophage library that displays peptide inserts on the minor (pIII) coat protein. This provides a high-throughput method for screening billions of different peptides against a biomaterial of interest. Such peptide libraries have been used for many applications including antibody-antigen binding interactions, mapping of protein-protein contacts, and determining peptide binding motifs for semiconductor materials such as ZnS, CdS, and GaAs. To our knowledge, this has never been done before for synthetic polymers, and would provide a major contribution to the field of biomaterials. In particular, we focused on polypyrrole, an electrically conductive polymer that has shown to enhance nerve regeneration, as a model biomaterial to select for unique peptide sequences for direct surface modification.

10:30 AM *H4.4
Conformational Genomics and Synthetic Biology. Jijun Dong[1,2], Kun Lu[1,2], Ken Walsh[1,2], Xiaoyu Li[1,2] and David G Lynn[1,2]; [1]Chemistry and Biology, Emory University, Atlanta, Georgia; [2]Center for Fundamental and Applied Molecular Evolution, Emory university, Atlanta, Georgia.

Amyloid, best known for its association with degenerative maladies including diabetes, prion disorders, Parkinson's and Alzheimer's diseases (AD), represents a supramlecular ordered protein assembly seemingly accessible to all polypeptide sequences. Control of the favorable energetics of association of such self-assembling nanoscale materials is critical for disease and applicable to nanotechnology. Here we report that diverse morphologies evolve from peptide solutions of the Alzheimer's Disease related Ab peptides. Different morphologies ranging from fibrils, sheets, helical ribbons, twisted ribbons, and nanotubes, emerge from nucleating clusters that propagate in the presence of free peptide. Physical stabilization of a nucleus or arresting its propagation dictates successful selection of a specific morphology. Nucleation can also drive covalent bond formation, stabilizing and further increasing the half-life of a selected structure. These initial steps towards a synthetic biology suggest a rich diversity of approaches emerging for the construction of supra-molecular self-assemblies that can be selected for desired functional properties.

11:00 AM *H4.5
Pushing The Self-Assembly Envelope To Mimic Biology's Materials And Functions. Samuel I. Stupp, Materials Science & Engineering, Northwestern University, Evanston, Illinois.

The functionality of biology is based largely on the folding code of proteins which creates nanoscale objects with defined shapes and surface chemistries, followed by further self-assembly among proteins and other biopolymers through noncovalent interactions to create more complex and larger objects. In specific environments these complex structures are able to trigger mineralization to create hard phase-soft phase composites, in . Other biological capabilities include self-limiting assembly, replication, reversibility, and covalent capture without loss of shape. This lecture will illustrate many of these processes in synthetic systems using a toolbox of large molecules that contain blocks with different properties. The types of blocks include, rigid, flexible, dendritic, hydrophobic, hydrophilic, or functionalized. We illustrate with these systems spontaneous mineralization of self-assembled templates, the formation of noncovalent nanoribbons with electronic conductivity, functionalization of carbon nanotubes, and the controlled formation of nanofibers with cell signalling capacity for regenerative medicine.

11:30 AM *H4.6
Dynamic Behaviors of Self-Assembling Peptide Materials: Nanofibers, Nanotubes, Nanovesicles. Shuguang Zhang, Center for Biomedical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Understanding of new materials at the molecular level becomes increasingly critical for a new generation of nanomaterials for nanobiotechnology, namely, the design, synthesis and fabrication of nano-devices at the molecular scale from bottom up. Basic engineering principles for microfabrication can be learned by understanding the molecular self-assembly and programmed assembly phenomena. Self- and programmed assembly phenomena are ubiquitous in nature. The key elements in molecular self-assembly are chemical complementarity and structural compatibility through noncovalent interactions. Numerous self-assembling systems have been developed ranging from models to study of protein folding and protein conformational diseases, to surfactant peptides, nano-surface engineering, and nanobiotechnology. Several distinctive types of self-assembling peptide systems have been developed. These self-assembling peptide systems are simple, versatile and easy to produce. These self-assembly systems represent a significant advance in the molecular engineering for diverse technological innovations. Vauthey, S. Santoso, S., Gong, H., Watson, N. & Zhang, S. (2002) Molecular self-assembly of surfactant-like peptides to form nanotubes and nanovesicles. *Proc.Natl.Acad.Sci.USA* **99**, 5355-5360. Santoso, S., Hwang, W., Hartman, H. & Zhang, S. (2002) Self-assembly of surfactant-like peptides with variable glycine tails to form nanotubes

and nanovesicles. *NanoLetters* **2**, 687-691. Zhang, S. Marini, D. & Hwang, W., Santoso, S. (2002) Design nano biological materials through self-assembly of peptide & proteins. *CurrentopinioninChemicalBiology* **6**, 865-871. von Maltzahn, G., Vauthey, S., Santoso, S. & Zhang, S. (2003) Positively charged surfactant-like peptides self-assemble into nanostructures. *Langmuir* **19**, 4332-4337. Zhang, S. (2003) Building from bottom-up. *MaterialsToday* **6**, 20-27.

SESSION H5
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Tuesday Afternoon, December 2, 2003
Back Bay B (Sheraton)

1:30 PM *H5.1
Virus Based Scaffolds for the Peptide Directed Synthesis of Single Crystal Magnetic and Semiconducting Nanowires and Liquid Crystals. Chuanbin Mao, Dan Solis, Seung-wuk Lee, Brian Reiss, Christine Flynn and Angela Belcher; Department of Materials Science and Engineering, Chemistry, and Biological Engineering, MIT, Cambridge, Massachusetts.

Peptides capable of specific recognition and nucleation of semiconductor and magnetic materials were isolated and engineered into advance biological viral templates and long range-ordering viral liquid crystal systems. Peptides selected through an evolutionary screening process, which exhibit control of composition, size and phase during nanoparticle nucleation were exploited for these materials-directing structures. The incorporation of specific, nucleating peptides into the generic scaffold of the M13 coat structure provides a viable template for the directed synthesis of semiconducting and magnetic materials. The engineered viruses were exposed to semiconductor precursor solutions, and the resultant nanocrystals that were templated along the viruses to form nanowires were extensively characterized using high-resolution analytical electron microscopy and photoluminescence. Removal of the viral template via annealing promoted oriented aggregation-based crystal growth, forming individual single crystal nanowires. We report a virus based scaffold for the synthesis of crystalline ZnS and the first free standing L10 CoPt nanowires. The unique ability to interchange substrate specific peptides into the linear self-assembled filamentous construct of the M13 virus introduces a material tunability not seen in previous synthetic routes. Additionally, liquid crystal systems were used for the fabrication of a highly ordered composite material composed of genetically engineered M13 bacteriophage and inorganic nanocrystals.

2:00 PM H5.2
Controlling Self-Assembly: How Assembly Conditions Affect the Micro and Nanostructure of Amphiphilic Diblock Polypeptides. Lisa M Pakstis[1,2], Andrew P Nowak[3,4], Timothy J. Deming[3,4] and Darrin Pochan[1,2]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Delaware Biotechnology Institute, University of Delaware, Newark, Delaware; [3]Materials, University of California, Santa Barbara, California; [4]Chemistry, University of California, Santa Barbara, California.

Self-assembling amphiphilic polypeptides are being studied as materials for biomedical applications. These low molecular weight amphiphilic polypeptides have a hydrophilic lysine (K) or glutamic acid (E) block and a hydrophobic leucine (L) or valine (V) block. Dissolution in aqueous solution at neutral pH and low fraction of polymer (vol. fraction polypeptide $\geq$ 0.5 wt%) allows the polypeptides to self assemble into hydrogels. When these polypeptides are dissolved in organic solvent and dialyzed against water, allowing the molecules to reach a kinetic equilibrium, the polypeptides form small micellular structures. Both the hydrogels and micelles have been studied using laser scanning confocal microscopy (LSCM) and cryogenic transmission electron microscopy (cryo-TEM) to allow for *insitu* characterization of the micro and nano structure, respectively, in solutions of varying ionic strength. The critical association concentrations (cac) of the polypeptides in either the gelation or micellular state, relative to the assembly pathway, as well as the micelle size and distribution, have been determined using dynamic light scattering (DLS) and atomic force microscopy (AFM). The feasibility of using these diblock polypeptides for biomedical applications has been assessed through cytotoxicity assays with fibroblasts. The pathway of polypeptide assembly determines the future applicability of these materials as either tissue engineering scaffolds in the hydrogel state or as gene delivery agents in the micellular form.

2:15 PM H5.3
Towards Functional Models of the Cytoplasm: Controlling Biomolecule Partitioning within a Cytomimetic Environment. Marcus Helfrich, Lauren Mangeney-Slavin, Karerra Djoko, Micheal Scott Long and Christine Keating; Chemistry, Pennsylvania State University, University Park, Pennsylvania.

The complex self-assembled structure of the biological cell is unique in its ability to simultaneously carry out multiple reactions in localized regions within the cytoplasm. Understanding how the chemical and physical properties of the cytoplasmic environment influence cellular organization and function opens the door for the possible development of "artificial cells" that could be tailored to carry out specific reactions on the nano or mesoscale. The research in our laboratory utilizes giant unilamellar phospholipid vesicles that have been filled with an aqueous two phase system (ATPS), comprised of two reversibly phase separating polymers, to model the cytoplasmic environment of the cell. Using an ATPS as a model cytoplasm allows the position and the reactivity of different biomolecule populations to be controlled within the phase system. The synthesis and characterization of these novel cellular mimics will be discussed as well as the partitioning behavior of the encapsulated polymers used to form the ATPS. The partitioning behavior and reactivity of various macromolecules, including DNA and several different enzymes, will also be presented.

2:30 PM *H5.4
Ultrathin Star-Polymer Layers for Proteinrepulsive and Biofunctional Interfaces. Martin Moeller, Institute of Technical and Macromolecular Chemistry, RWTH Aache University of Technology, Aachen, Germany.

We prepare star poly(ethylene oxide) (PEO) hydrogel layers that provide a well-defined bioactive interface to study the adhesion and proliferation of tissue cells. The hydrogels can be assembled molecular layer-by-layer from multifunctional PEO-stars, which allows the formation of a well-defined biologically inert interface that resists the non-specific adsorption of cells and/or proteins. Functionalization of the hydrogels with PEO-stars containing specific peptide ligands allows receptor-mediated cell-adhesion. By combination of lithographic techniques, block copolymer templating and solid-phase synthesis, the concentration, spatial distribution and clustering of the peptide ligands can be precisely controlled over length scales ranging from several nanometers up to a few micrometers. The result is a unique model system that allows a systematic study of cellular behaviour in response to (bio)chemical, topological and mechanical stimuli.

3:30 PM H5.5
Self-Assembled Peptide Functionalized Hydrogels. Stefano Tugulu[1], Harm-Anton Klok[1], August Bernd[2], Martin Moeller[3], Juergen Groll[3] and Joachim Spatz[4]; [1]Institut des Materiaux, Laboratoire des Polymeres, EPFL, Lausanne, Switzerland; [2]Zentrum der Dermatologie und Venerologie, Klinikum der Johann Wolfgang Goethe-Universitaet, Frankfurt, Germany; [3]Deutsches Wollforschungsinstitut, RWTH Aachen, Aachen, Germany; [4]Physikalisch-Chemisches Institut, Biophysikalische Chemie, Universitaet Heidelberg, Heidelberg, Germany.

Integrin mediated cell adhesion is crucial for proper cell function and plays a major role in the regulation of cell proliferation, differentiation and apoptosis. Integrins also play a major role in the mechanosensory system, enabling cells to sense the topology and mechanical properties of their environment as well as to detect mechanical stimuli. The main events in the function of this mechanosensory system are the binding of integrins to extracellular ligands, the clustering of integrins in the plane of the cell membrane and the aggregation of signalling molecules, linker proteins and other transmembrane receptors for extracellular signalling molecules. The resulting protein complexes, known as focal adhesion complexes, transduce the mechanical stimulus into a chemical signal, which results in an alteration of the expression of specific gene products. A systematic investigation of the (combined) effects of (bio)chemical, topological and mechanical stimuli on integrin dependent cellular behaviour requires the use of a well-defined model system. We present a model system, which allows the investigation of the combined effects of topological, mechanical and chemical stimuli on cell adhesion and proliferation. The model system consists of a PEO-PPO hydrogel prepared by self assembly of cross-linkable multifunctional starpolymers. A layer of this hydrogel is deposited on an elastic PDMS support resulting in a substrate bearing an intrinsically bioinert surface resistant against non-specific adsorption of cells and proteins and enabling the mechanical deformation of the resulting substrate in elongation experiments. Cell adhesion e.g. integrin specific adhesion on this substrate can be achieved by functionalizing its surface with peptide ligands acting as recognition motifs. In this contribution, we will present several complementary approaches, which allow precise control over the concentration, spatial distribution and clustering of peptide ligands over length scales ranging from several nanometers up to a few micrometers.

3:45 PM H5.6
Patterning of two component biological colloidal particle

arrays atop polymer multilayers. Haipeng Zheng, Michael F. Rubner and Paula T. Hammond; MIT, Cambridge, Massachusetts.

New approaches to pattern biofunctional polymer-colloid templates for selective cell attachment utilizing soft lithography and selective deposition techniques on polyelectrolyte multilayer thin films will be presented. The surface of poly(acrylic acid) /poly(allylamine hydrochloride) multilayer films was constructed specifically to prevent cell adhesion; while a cell-adhesive colloidal array was achieved by the chemical modification of colloidal particles with RGD peptides. In this work, two component colloidal arrays including cell-inert and cell-adhesive colloidal arrays atop polymer multilayer films were also designed to direct cell attachment. The effects of pattern geometry, surface topography and particle functionality on cell spreading were studied. In order to understand the interactions between cells and colloidal particles, confocal images and fibroblast focal adhesion and actin stress fibers on different colloidal templates were investigated. The control of cell behavior in such micropatterned biological material systems can offer the capability to fabricate cell-based biosensors, tissue engineered scaffolds, and drug screening devices.

4:00 PM *H5.7
Peptide Mediated Surface Modification for Controlling Cell-Material Interactions. Phillip Messersmith, Jeffrey Dalsin and Lijun Lin; Biomedical Engineering, Northwestern University, Evanston, Illinois.

Certain marine organisms secrete remarkable protein-based adhesive materials for adherence to the mineral, metal, and wood surfaces upon which they reside. For example, mussel adhesive proteins (MAPs) contain L-3,4-dihydroxyphenylalanine (DOPA), an amino acid that is believed to be responsible for the adhesive characteristics of MAPs. Although the exact role of DOPA in these proteins is not known, recent evidence suggests that interfacial adhesion to substrates is generally believed to be due to chemical interactions between DOPA and functional groups at the surface of the solid substrate. In this presentation we will describe our efforts to exploit the adhesive qualities of DOPA containing peptides to control cell behavior at surfaces. Our strategy for accomplishing this utilizes simple solution modification of material surfaces by conjugates of DOPA-containing peptides and the nonfouling polymer poly(ethylene glycol) (PEG). Characterization of the modified surfaces by XPS, TOF-SIMS and other methods indicates that the nonfouling PEG polymer is anchored onto the surface by the DOPA containing peptide. For example, exposure of a variety of material surfaces (e.g. gold, titanium, stainless steel, etc.) to a solution of DOPA-PEG polymer results in deposition of PEG onto the surface as well as significantly reduced protein and cell adsorption to the surface. Obvious applications of this strategy include protein and cell-resistant surfaces for medical applications (biosensors, coagulation-resistant surfaces, etc.), however there is considerable potential use of this strategy for nonmedical applications as well. Finally, we will also describe our efforts to use this approach to facilitate specific cell-surface interactions, by appending RGD or other ligands for cell surface receptors, onto the terminus of the PEG chain.

4:30 PM *H5.8
Exploitation Of Collagen Mimetic Peptide As A Collagen Adhesive Biopolymer For Novel Biomaterials Development. Seungju M. Yu[1,2], Allen Yi-Lan Wang[1] and Chang-Soo Yun[1]; [1]Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; [2]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland.

Collagen, either alone or in combination with other component, is an important biomaterial that is used in a variety of medical applications ranging from hemostatic materials and biocompatible coatings to drug delivery and tissue engineering. Currently, there are manifest biomedical interests in modifying the structure of natural collagen to improve its biochemical and mechanical properties. As an alternative to the prevalent "chemical" modification method, we have developed a novel "physical" collagen modification technique that is based on collagen's native ability to fold into triple-helix molecular architecture. Here we present that synthetic collagen mimetic peptides exhibit specific affinity to natural collagen under controlled thermal conditions (heat or laser treatment). Such affinity can be explored as a new targeting method to attach therapeutic drugs to collagens in the living tissues and to biomaterials that incorporate natural collagens.

SESSION H6: Poster Session II
Chairs: Annelise E. Barron, Timothy Deming and Harm-Anton Klok
Tuesday Evening, December 2, 2003
8:00 PM
Exhibition Hall D (Hynes)

H6.1
Magnetic Nanosensors for the Detection of Molecular Targets. J. Manuel Perez, Lee Josephson and Ralph Weissleder; Center For Molecular Imaging Research, MGH-Harvard Medical School, Charlestown, Massachusetts.

Nanomaterials may be useful for the development of highly-sensitive and high-throughput biosensors required for genomic and proteomic data acquisition in complex biological samples and potentially for in vivo applications. One particular challenge has been to develop biocompatible systems that a) can be miniaturized b) allow measurements in turbid/obscure media, c) require minimal sample preparation, d) allow fast sample throughput and e) can potentially be applied for in vivo imaging. We have developed a novel magnetic nanosensor technology fulfilling these prerequisites for molecular target detection in biomedical applications. The technique uses magnetic nanoparticles that selectively change the spin-spin relaxation times (T2) of surrounding water molecules upon specific molecular target interaction. In preliminary studies we have shown that when monodisperse magnetic nanoparticles self-assemble into stable nanoasemblies of 300-500 nm, there is a corresponding decrease in the spin-spin relaxation times (T2) of surrounding water detectable by NMR techniques. We have found that the technology can be used to sense DNA/RNA, protein, and enzymatic activity without extensive sample purification or amplification from biological samples. The current detection threshold of the technology is in the subfemtomole range for DNA with extremely high molecular specificity. The assay is performed in solution and does not require isolation or purification of the sample. Major biotechnical and medical applications of the developed technique lie in 1) the development of techniques to simultaneously interrogate RNA and proteins, 2) the development of high-throughput solution phase arrays and 3) the ability to image molecular interactions by magnetic resonance imaging. Furthermore, because the magnetic nanoparticles are fully biocompatible, the technology may ultimately allow in vivo sensing. We will present data showing the ability of the developed technique to sense various targets such as GFP (mRNA and protein), telomerase (mRNA, protein and activity), DNA cleaving agents, proteases and intact viruses (herpes simplex and adenovirus).

H6.2
Self Assembling Model Lipid Membranes for Investigating Irritation in Skin. Srividya Ramakrishnan[1], David Moore[1] and Eilidh Bedford[2]; [1]Unilever Research, Edgewater, New Jersey; [2]Unilever Research, Port Sunlight, United Kingdom.

The objective of this work was to identify suitable microstructural biomimetic models for topically induced skin irritation and develop anti-irritation technologies based on this understanding. The outer layer of skin, the stratum corneum (SC), provides the body with a formidable barrier to the ingress of foreign molecules. The SC consists of a complex microstructure of highly ordered lipid mesophases surrounding protein-rich cells. These ordered lipid phases are responsible for the skin's barrier function. Disruption of the SC's lipid structure compromises barrier function, often resulting in dermatological irritation. The current study focuses on retinoids, a widely used class of dermatological actives, which can induce irritation when topically applied. A model of the SC lipid matrix consisting of the SC's major lipid species, ceramides, cholesterol and fatty acids, was used to study the effect of retinoids on the complex microstructure of the SC. Lipid organization was investigated using X-Ray, DSC, and FTIR spectroscopy. When necessary deuterated stearic acid was used to spectroscopically distinguish the ceramide and fatty acid signals in the FTIR spectra. The FTIR results demonstrated that ceramides and fatty acids, in the above-described model, exist in separate orthorhombically packed phases within a complex lamellar mesophasic matrix. Consistent with this, we observed that the ceramide and fatty acid phases disorder at different temperatures. The addition of retinol to our SC lipid model caused disordering of the lipid bilayers, as evidenced by the lower lipid disordering temperature of the ceramides and fatty acid, as measured both by FTIR and DSC. Disruption in lipid microstructure and phase behavior, was dependent on retinol concentration, but was still significant at concentrations as low as 1.5mol%. Similar changes in lipid behavior have been observed in intact porcine SC samples when treated with retinol. We are currently investigating the potential biophysical mechanism of borage seed oil, a clinically effective topical anti-irritant. Our recent results demonstrate that SC treated with retinol, and subsequently with borage seed oil, recovered its original lipid microstructure, suggesting one possible mechanism for reducing irritation is to control SC lipid microstructure.

H6.3
Bio-inspired Periodic Microlens Arrays Created by Multi-beam Interference Lithography. Shu Yang[1], Mischa Megens[1,2] and Joanna Aizenberg[1]; [1]Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey; [2]Philips Research

Laboratories, Prof. Holstlaan 4, NL-5656AA Eindhoven, Netherlands.

Nature has developed strategies that give biological processes and structures exquisite selectivity and performance. Inspired by the discovery of light-sensitive brittlestars, which have microlens arrays with integrated pores, we develop a novel, yet simple approach that uses holographic lithography to create porous lens arrays that are analogous to the biological structures. In comparison, microstructures fabricated by conventional photolithography do not form such lens arrays. Further, we will discuss possibilities to tune the optical properties in the artificial microlens arrays.

H6.4
An All-Solid State Electronic Wettability Switch Based on a Combination of Electro-Active Organic Materials.
Magnus Berggren, Joakim Isaksson and Nate Robinson; ITN, Linkoping University, Norrkoping, Sweden.

Here we report on a solid-state device having an electro-active surface being exposed to the surrounding environment. The surface tension properties of this surface can be updated electronically. This is achieved via including an electronically updateable surfactant in a solid-state device. Upon addressing the device electronically, the surfactant exposes a hydrophilic or a hydrophobic molecular subsistent outward of the surface. This causes a change of the surface tension of the active surface. We have characterized the electronic wettability switch with surface sensitive analytical tools and simple with water contact angle measurements. The switch of the contact angle is large indicating that the switching mechanism is fairly efficient. Controlling the surface tension is known to play an important role for cell-growth, adsorption of biomaterials and for controlling the dynamics of fluids. We will describe the principal function of this device and its possible use as a "control device" of the growth and assembly of liquid and solid state formations.

H6.5
Abstract Withdrawn

H6.6
The design of self-assembled multivalent nanoparticles.
Alvaro Carrillo and Ravi S. Kane; Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York.

We describe the synthesis and characterization of self-assembled nanoparticles based on ring-opening metathesis polymerization (ROMP). Biofunctionalized nanoparticles may form the basis of a new class of potent multivalent antagonists, molecules that bind to pathogens or toxins and prevent their attachment to target cells. These antagonists may contribute to therapies for diseases including AIDS, anthrax, and cholera. The formation of colloidal nanoparticles of controlled size is also important for applications in drug delivery and for the control of biological interactions. Hydrophobic and hydrophilic derivatives of norbornene were synthesized as monomers and then polymerized using the Grubbs catalyst (Cl2Ru(CHPh)(PCy3)2) to form diblock copolymers of controlled composition. The polymers were characterized using nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Tuning the composition of the block copolymer enables the tuning of the diameters of the self-assembled nanoparticles in the 5-100 nm range. The nanoparticles were characterized using dynamic light scattering (DLS) and scanning electron microscopy (SEM). The functionalization of the nanoparticles with biological ligands will also be discussed.

H6.7
Biocomposite Nanoarchitectures with Gas-Phase Bioactivity.
Jean Marie Wallace[1], Jane K Rice[1], Kristin B Eden[1], Rhonda M Stroud[2], Jeremy J Pietron[1], Jeffrey W Long[1] and Debra R Rolison[1]; [1]Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; [2]Surface Modification Branch, Naval Research Laboratory, Washington, District of Columbia.

Multifunctional composite aerogels-highly porous, high-surface-area materials-can be formed by "nanogluing" appropriate guests into the network of an about-to-gel silica sol [1]. Recent results indicate that biocompatibility can also be engineered into the supercritical-fluid-processed silica aerogel nanoarchitecture. We encapsulate the heme protein, cytochrome *c*, within a silica nanoarchitecture by nanogluing a protein-protein superstructure (nucleated in the liquid phase by colloidal gold) into the three-dimensional gel. The superstructure provides stability to the protein in solution, as shown by a shift in the pK of unfolding in the presence of a chemical denaturant. The entrapped cytochrome is also stabilized to the harsh conditions necessary to produce an aerogel, as evident by retention of the Soret band. The protein binds gas-phase NO and remains in a stable configuration within the silica matrix for *ca.* 6 weeks at room temperature, as long as the ambient humidity is kept high. Further investigations are probing the properties of the protein-protein superstructure by varying the size and type of metal colloid and the protein itself. These studies will provide fundamental information on the interactions between biological entities and metal oxide hosts. [1] C.A. Morris, M.L. Anderson, R.M. Stroud, C.I. Merzbacher, D.R. Rolison, *Science*, **284**, 622 (1999).

H6.8
Cell Interactions with Polyelectrolyte Thin Films.
Hyo Sook Jung[1], J. S. Koo[1], Kwanwoo Shin[1], Ju Myung Song[2] and Joon-Seop Kim[2]; [1]Materials Science and Engineering, Kwangju Institute of Science and Technology, Gwangju, South Korea; [2]Polymer Science and Engineering, Chosun University, Gwangju.

Random polyelectrolyte films have been shown to have numerous applications as biomimetic materials. Polymers with relatively low ionic content (less than 30 mole %) have been shown to achieve charge concentrations comparable to those in the extra-cellular matrix. The interaction between the cells and charged surface can be strongly influenced by 1) the presence of ions in a buffer solution due to the electrostatic interactions, and 2) the hydrated surface dynamics due to the presence of diffused surface morphology with varying surface charge densities. Here we report on image ellipsometry and microscopic study where we explore the interactions and in situ dynamics of the fibroblast cells on the polyelectrolyte layer, in this case sulfonated polystyrene (PSSx.) and polystyrene acrylic acid(PSAAx). The adsorption/desorption behavior of fibroblast cells are found to be quite difference as a function of degree of charges. These results are then correlated with systemic study of the adsorption dynamics of cells as a function of incubation time for various charge densities of the polyelectrolytes. This work was supported by Korea Research Foundation.

H6.9
Modeling the structure and electrostatics of a DNA/carbon nanotube hybrid. Anand Jagota, Steve Lustig and Ming Zheng; DuPont, Wilmington, Delaware.

The recently discovered ability of ssDNA to form a stable hybrid material with single walled carbon nanotubes has proved extremely useful in forming stable dispersions, and in providing routes for their separation according to electronic structure and diameter. The hybrid is stabilized by stacking interactions between the bases and the nanotube surface, and solubilized in water by the exposed phosphate groups. We present detailed molecular modeling of the sequence-dependent structure of the DNA/nanotube hybrid using molecular statics, dynamics, and Monte Carlo simulations. Sequences can stack as single strands, or double strands stabilized by inter-strand hydrogen bonds. We have additionally modeled the process of elution of the hybrid material from a charged substrate, the basis of our separation technique, using classical electrostatics. Our model describes the elution process as competition between the bound and eluted state with condensed counter ions, and predicts critical salt concentration within the range of experimental values that is sensitive to the type of carbon nanotube embedded in the DNA wrap.

H6.10
Development of Fibrin-free Intraocular Lens for Blocking After-cataract with Photochemical Surface Modification.
Katsuya Tanizawa, Yuji Sato and Masataka Murahara; Electrical Engineering, Tokai Univ., Hiratsuka, Japan.

The hydrophilic and hydrophobic groups were substituted alternately on a PMMA intraocular lens (IOL) surface with photochemical reactions of ArF excimer laser and Xe_2 excimer lamp.Thus, the IOL was developed that is free from fibrin. In operative treatment for cataract, an IOL is generally implanted instead of the cloudy crystalline lens. However, fibrin is stuck onto the IOL surface after long-term insertion, and cells proliferate on it, which makes the IOL surface gets opaque; that is after-cataract. Accordingly, we designed the micro domain structure of hydrophilic and hydrophobic groups on the IOL surface for fibrin-free. Firstly, the IOL was irradiated with Xe_2 excimer lamp in the presence of perfluoropolyether to be hydrophobic. By this photochemical reaction, the CF_3 functional groups were substituted on the IOL surface. Secondly, the ArF laser was projected through the mask pattern in reduced size in the presence of water on IOL surface to be hydrophilic. By this photochemical reaction, the OH functional group was substituted at the exposure part. Microscopic infrared spectroscopy analysis was carried out to investigate the hydrophilic or hydrophobic groups that had been substituted on the IOL. Therefore, it became clear that CF_3 and OH radicals were substituted in the interval of 100μm on the IOL surface. Fibrin sticking test was carried out with FT-IR and SEM. As the result, it is clarified that the fibrin sticking rate of the sample, which treated at the 8 minute irradiation of Xe_2 lamp for hydrophobic treatment and laser fluence of 20mJ/cm^2 with laser shot number of 6000 for patterned hydrophilic treatment, decreased 23% compared with non-treated sample. In these experimental results, the micro

domain structure of hydrophilic and hydrophobic groups inhibits the fibrin sticking rate. In conclusion, the production of the ideal intraocular lens was demonstrated.

H6.11
Semiconductor-metal quantum-dot super-molecules: light emission and energy transport. Nicholas Alexander Kotov[1], Alexander Govorov[2], Jim Lee[1] and Ying Wang[1]; [1]Chemistry, Oklahoma State University, Stillwater, Oklahoma; [2]Physics, Ohio University, Athens, Ohio.

Hybrid semiconductor-metal supramolecules have been fabricated by using antigen-antibody and biotin-streptavidin affinity. When the distance between the supramolecule elements is optimized, Au nanoparticles (NP), strongly enhance (5-10 fold) the excitonic light emission of CdTe NP and nanowires (NW). The diameters of NP and NW were chosen to effect the resonance condition between plasmon adsorption of Au NP and excitonic emission of CdTe colloids. The enhancement effect is explained in terms of plasmon-assisted absorption of incident light and plasmon-induced increase of nanoparticle dipole moments. Both experimental and theoretical analysis of this mechanism will be discussed. Calculations show that the enhancement of emission comes from plasmon-enhanced optical fields in the vicinity of semiconductor nanocrystals. Qualitative agreement with experimental data was obtained when single NP/NW is surrounded by several Au-NPs. TEM images demonstrate that that 3-4 and 10-15 Au NP are attached to CdTe NP and NW, respectively. The effect of enhanced luminescence is comparable to the surface enhanced Raman scattering and can be taken advantage of in optoelectronic nanoscale devises and biological sensors.

H6.12
Large Scale Thermal Undulations of a Lipid Membrane using an Implicit Solvent Model. Brendan O'Malley[1], Federico Meneghini[2] and Massimo Noro[1]; [1]Unilever Research and Development, Bebington, United Kingdom; [2]University of Padua, Padua, Italy.

Lipid membranes undergo thermal undulations that influence both their elastic properties and surface tension. Recent theoretical studies have suggested that the effect of these thermal undulations is to stiffen the membrane, while computer simulation studies of lipid membranes at the atomic level have indicated that the absence of long wavelength undulations in these nanometre scale simulations leads to a larger surface tension than would be expected at a macroscopic level. This study uses the dissipative particle dynamics (DPD) method to simulate simple model membranes composed of one or more different lipid molecules. The influence of the size of the membrane patch simulated on the observed thermal undulations and the effect on related macroscopic properties are the main focus of this work. In order to probe length scales on the order of a micron we propose an implicit solvent model in which the effect of the solvent on the lipid molecules is replaced by a many-body lipid-lipid interaction. A dipole-dipole like interaction between surfactant molecules is employed to produce a stable monolayer of lipid while a simple attractive term between lipid tails is used to produce a stable bilayer. The results of this study and also of complementary DPD studies including solvent will be presented. Lastly the effect of lipid composition on the elastic properties and surface tension of our simple model membrane will be described.

H6.13
Patternable PEG grafted poly(allylamine) for fabrication of bio-array templates. Heejae Kim[1], Junsang Doh[2], Darrell Irvine[1], Robert Cohen[2] and Paula Hammond[2]; [1]Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Newly designed poly(allylamine)-g-poly(ethylene glycol) polycation graft copolymers have been synthesized in order to combine bio-functionality with the ability to pattern charged polyelectrolyte multilayer surfaces. Polymer-on-polymer stamping (POPS) techniques developed in our group have been used successfully to produce micron scale patterned regions on negatively charged multilayer surfaces by direct stamping of these PEG grafted poly(allylamine) copolymers, even when the fraction of grafted PEG in the copolymer dominates the composition. As is well known, the long side chains of PEG effectively resist adsorption of antibodies or other proteins, and create a bio-inert area when patterned by POPS. On the other hand, a desired antibody can be covalently attached to the graft copolymer by introducing proper coupling agents at the end-functionalized PEG side chain. In this way, a pattern of a specific antibody can be achieved without random, non-specific adsorption of other proteins. Generation of the antibody pattern can directly lead to fabrication of a patterned cellular array. In this study, we investigated properties of the new graft copolymer and utilized it to make cellular arrays as well as protein arrays.

H6.14
Assembly of Polysaccharide-Derivatized Polymer Networks for Protein Delivery. Nori Yamaguchi[1,2] and Kristi L Kiick[1,2]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Delaware Biotechnology Institute, Newark, Delaware.

The paradigm of modern biomaterials research is the design of polymeric materials that can respond to specific stimuli and provide a desired biological response. Polymeric materials have been produced that can deliver therapeutic molecules in response to stimuli such as pH, temperature, hydrolysis, or enzymolysis, and scaffolds that can direct the proliferation of cells and tissue have become increasingly important in tissue engineering. We propose a novel strategy for the assembly of hydrogel networks and subsequent delivery of polypeptide molecules in response to specific cells, via the use of heparin-functionalized polymers whose assembly, rheological properties, and delivery profiles are controlled by specific protein-saccharide interactions. Heparin-decorated polymers, synthesized by reacting thiol end-terminated multiarm poly(ethylene glycol)s (MW 10,000) with maleimide functionalized heparin (MW 3000), have been characterized by 1H NMR spectroscopy, size-exclusion chromatography, and dynamic light scattering; results indicate attachment of heparin with at least 75% efficiency. Hydrogels have been formed on the basis of the interaction of these polymers with heparin-binding macromolecules, and the viscoelastic properties of these hydrogel networks have been measured by optical probe microrheology and bulk rheology methods. The binding and release of polypeptide growth factors to these heparinized hydrogels has also been demonstrated via immunochemical assays. The combination of these results suggests the opportunities for assembling novel networks on the basis of protein-saccharide interactions, and employing these networks for drug delivery applications.

H6.15
Functional Cytomimetic Materials Through Aqueous Phase Separation. Michael Scott Long, Marcus R Helfrich and Christine D Keating; Chemistry, Pennsylvania State University, University Park, Pennsylvania.

The cellular cytoplasm is a complex environment in which biomolecules are localized within distinct domains, the mechanism of which is not clear. One theory to explain macromolecular localization involves aqueous phase separation, a physical phenomenon in which two polymers separate into distinct domains at low weight percents but remain soluble in water. Partitioning of biomaterials within different phases of bulk aqueous two-phase systems (ATPS) has been widely documented towards non-denaturing separation. This work describes the use of immiscible ATPS as a simplified synthetic analog of the cellular cytoplasm. We have observed the temperature-dependent phase behavior of ATPS in bulk and have used this information to encapsulate ATPS within synthetic phospholipid vesicles (typically 5-50 microns). We have found that aqueous phase separation within lipid vesicles does not necessarily follow bulk behavior; it is dependent on the lipids used for vesicle preparation as well as the identity and concentration of the external diluent used for microscopic imaging. Lipid vesicles comprised of varying ratios of DOPC:DOPG:DOPE-PEG 2000 typically do not exhibit aqueous phase separation even when it is predicted from bulk behavior, requiring a hypertonic sucrose solution to display this phenomenon. We have partitioned proteins within bulk ATPS and lipid vesicles, finding that the two exhibit differing behavior. Typically, partitioning within lipid vesicles occurs to a lesser extent than that predicted by bulk behavior.

H6.16
Select Increased Neuronal Cell Function on Nanoporous Silicon. Janice L McKenzie[1], Marisa A Sambito[2], Nader M Kalkhoran[2] and Thomas Jay Webster[1]; [1]Biomedical Engineering, Purdue University, Lafayette, Indiana; [2]Spire Biomedical Corporation, Bedford, Massachusetts.

Nanotechnology can be defined as using materials whose components exhibit novel properties by gaining control of structures at the atomic, molecular, and supramolecular levels. Although many advanced properties of materials with constituent particle sizes less than 100 nm have been observed for traditional science and engineering applications, very few advantages of these materials have been explored for tissue-engineering. Nanophase materials may give researchers control over interactions with biological entities (such as proteins and cells) in ways previously unimaginable with conventional materials. This is because organs of the body are primarily made of nanostructures and, thus, cells in the body are accustomed to interacting with materials which have similar feature sizes. For example, laminin (a protein approximately 70 nm in width and length) is a common extracellular matrix component of neural tissue.

Despite this fact, implants currently being investigated for neural applications (such as silicon) do not possess a large degree of nano-structured surface features. To test the hypothesis of using nanostructured materials as neural implants, in the present study, we synthesized biocompatible layers of nanoporous silicon using an electrochemical etch process. Furthermore, we utilized these nanoporous silicon layers as templates for growth of aligned carbon nanofibers using chemical vapor deposition. Cell culture experiments were performed with astrocytes (glial scar tissue forming cells) and neurons to test the ability of such materials to serve as neural implants. Results from these studies suggest enhanced interactions of neurons on nanoporous silicon as compared to smooth silicon surfaces. In contrast, the nanoporous silicon material appeared to show less interaction with astrocytes, as compared to smooth silicon. This study thus clearly indicates that nanostructured porous silicon materials can be used to significantly enhance select functions of neurons important for neural tissue engineering applications. This work was supported in part by NSF Grant No. DMI-023259.

H6.17
Mesoscale simulation studies of chiral self-assembly.
Robin Selinger[1,2], Jonathan V. Selinger[2] and Joel M. Schnur[2]; [1]Physics Dept., Catholic Univ., Washington, District of Columbia; [2]Ctr for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, District of Columbia.

Under the right temperature and concentration conditions, amphiphilic lipids in solution self-assemble to form chiral supramolecular aggregates including tubules and twisted or helical bilayer ribbons. Shape selection during self-assembly is driven by the interplay of elasticity and chirality, and by solution properties including hydrophobic and hydrophilic interactions. We have developed an efficient mesoscale simulation technique to model the growth of a chiral bilayer ribbon, enabling us to explore systematically the shape selection process as a function of the membrane's elastic and chiral properties. We find that small changes in either stretch or bend elastic moduli drive transitions in aggregate morphology, and that a change in the tilt direction–but not the chiral nature–of the bilayer can reverse the handedness of the aggregate. We compare our results with those of recent experiments.

H6.18
Effect of the Crystallization Chamber Design on the Polymorphs on the Calcium Carbonate Using thye Sitting-Drop Method. Andronico David Neira[1,2], M S Fernandez[1], J Retuert[2] and J L Arias[1]; [1]Faculty of Veterinary and Animal Sciences, University of Chile, Santiago, Santiago, Chile; [2]Departament of Basic Chemistry, University of Chile and Center for advanced Interdisciplinary Research in Materials, Santiago, Santiago, Chile.

The precipitation of CaCO3 is widely occurring process in nature (biomineralization) as well as an important operation in industry.CaCO3 nucleates in three crystalline polymorphs: calcite, aragonite and vaterite. Biological systems control polymorphism by the production of particular macromolecules or by regulating diffusion rate of inorganic components. Although the effect of experimental variables on the polymorphs has been studied by number of authors, the favorable conditions for getting each polymorph are generally uncertain.Aragonite is less abundant than calcite and is formed under a very narrow range of physicochemical conditions and is easily transformed into calcite by changes in the environment. Nowadays, the interest in aragonite has increased substantially. Its needle-like crystals are used as fillers for the improvement of mechanical properties of paper and polymer materials. In this work we have studied CaCO3 crystallization using sitting-drop method at different temperatures. The crystallization experiments were done using a chamber consisting of 85 mm plastic Petri having a central hole in its bottom glued to a plastic cylindrical vessel. Inside the chamber, micro-bridges were filled with 35 uL of 200mM CaCl2 solution in 200mM TRIS buffer pH 9. The central hole allows the diffusion of CO2 vapor from the (NH4)HCO3 into the buffered CaCl2 solution on the polymorphism of CaCO3. Variying the hole diameter of the CaCL2-containing chamber, its distance from the CO2 source and the temperature of the experiments this rate was changed. The hole diameter was varied from 3 mm to 30 mm, the distance between 15 mm to 105 mm and the temperatures from 20 to 70 C. In case of hole diameter of 30 mm a kinetic crystallization experiment at 70 C for variable periods of time (3-48 h)were done. Experiments were carried out increasing anddecreasing the diameter of the central Petri dish. It was found that by diminishing the distance between the ammonium carbonate and calcium chloride solution, and by increasing the hole diameter and/or the temperature, a notorious increase in the aragonite form is observed. By combining these factors appropriately even vaterite crystals were obtained. Since the kinetic of crystallization is a determinant factor of the morphology, a convenient design of the crystallization chamber can conduct the crystallization of CaCO3 towards a specific crystalline form.

H6.19
Tobacco Mosaic Virus as a Template for Nanochemistry.
Stacey Jones-Willy[2,1], Neal R Armstrong[1] and Wei Xia[1]; [1]Chemistry, University of Arizona, Tucson, Arizona; [2]Biochemistry and Molecular Biophysics, University of Arizona, Tucson, Arizona.

Virus particles have recently been shown to be good templates for the growth of nanometer-scale objects with either metal or semiconductor coatings. Tobacco Mosaic Virus(TMV) is an excellent candidate for this purpose, given its well-defined structure (wirelike), its dimensions (ca. 300 nm in length and ca. 18 nm in width), and the ease of imaging by electron microscopy (SEM) and/or scanning probe microscopies (SPM). We show here that in addition to these attributes, it is possible to micro-contact print reasonably ordered thin films of TMV onto freshly cleaved mica substrates, with retention of orientation in the soft-lithography stamp. Optimization of the following parameters: 1) careful choice of solution deposition conditions (pH, TMV concentration), 2) the presence or absence of other proteins to prevent aggregation, 3) incubation of the soft-polymer stamp with the virus solution and careful drying, provide for "stamping" of the virus onto the mica surface with orientation of the virus preferentially along the long axis of the features embossed into the stamp (sub-micron line widths). SPM and SEM characterization of these features will be presented, along with prelininary results concerning the metallization of these virus-stamped surfaces.

H6.20
Novel Colloidal Amphiphilic Chitosan Nanospheres.
Rangrong Yoksan[1], Mitsuru Akashi[2] and Suwabun Chirachanchai[1]; [1]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Bangkok, Thailand; [2]Graduate School of Engineering, Osaka University, Osaka, Osaka, Japan.

Chitosan is accepted as one of the polysaccharides for the uses in pharmaceutical, biomedical, and agricultural fields due to the qualified properties of biodegradability, biocompatibility, bioactivity and non-toxicity, etc. Up to now, chitosan prodrugs are achieved easily from the simple processing such as film and membrane casting, gel formation, and bead preparation. In most cases, the sustained releases related to the random crosslinking network and the safety of crosslinker are always questioned. Although the drug conjugation with chitosan via chemical reaction is another way for chitosan prodrugs, the harsh reactions and the risk to loss drug active site have to be concerned. Drug incorporation with chitosan spheres without any reaction is an effective way to obtain prodrugs. Recently, there have been reports about chitosan spheres prepared from processing techniques with the sizes of 10∼700 mm [1]. However, this preparation might have to be studied in more details about the toxicity of crosslinker, the controlling of particle size, and the drug incorporation effectiveness. Herein, we summarize the strategy to obtain novel chitosan nanospheres without any specific processing technique [2]. The presentation will clarify the modification of chitosan under the concept of controlling hydrophobicity and hydrophilicity in the structure of N-phthaloylchitosan grafted mPEG. The study also covers the colloidal phenomena in various media. The presentation will discuss about the factors to control the nanosphere size and shape as well as the structure clarification by SEM, TEM, DLS, and ESCA.

H6.21
Silk Composites: Apatite Coated Electrospun Silk Fibers.
Chunmei Li[1], Hyoung-Joon Jin[2,1], Gregory D. Botsaris[1] and David L. Kaplan[1]; [1]Department of Chemical and Biological Engineering, Tufts University, Medford, Massachusetts; [2]Department of Polymer Science and Engineering, Inha University, Incheon, South Korea.

Human bone is a three-dimensional composite made of inorganic apatite crystals and organic collagen fibers. Mimicking this composite structure and composition has attracted interest for bone biomaterial substitutes and well as for materials design strategies in general. An attractive strategy to fabricate this kind of composite is to grow a layer of bone-like apatite on polymeric materials to generate osteoconductive features combined with good mechanical strength. Recent interest in the use of silk in biotechnological materials and in biomedical applications has derived from the unique mechanical properties, biocompatibility and biodegradability. For example, we have reported silk protein-based matrices for ligament and bone tissue engineering. Electrospinning offers an alternative approach to protein fiber formation that can potentially generate nanometer scale diameter fibers, a useful feature in some biomaterial and tissue engineering applications. In the present study, we explored the preparation of apatite-silk composites by growing apatite on functionalized nanodiameter silk fibers prepared by electrospinning. Functionalized fibers were spun from an aqueous solution of silk/PEO (80/20, wt/wt) containg poly-L-aspartic acid. An alternate soaking process was used to grow apatite on the fibers. The deposited apatite was characterized by scanning electron microscopy (SEM), X-ray

diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and X-ray Energy-Dispersive Spectroscopy (EDS). The amount of apatite deposited increased with increased soaking cycles and length of soaking. The aligned growth of hydroxyapatite preferentially parallel to the longitudinal direction of fibers was obtained when poly-L-aspartic acid was blended concentration at 200mg/g silk. EDS and XRD analysis showed that the mineral deposits were hydroxyapatite. The aligned growth of hydroxyapatite was probably due to the formation of banded gel-like structures of silk-poly-L-aspartic acid complexes along the fiber axis.

H6.22
Thin Film Modification for Bio-inspired Dynamic Microfluidic Lenses. Nicole Justis[1] and Yuh-wa Lo[2]; [1]Materials Science and Engineering, University of California - San Diego, La Jolla, California; [2]Electrical Engineering, University of California - San Diego, La Jolla, California.

Bioinspired dynamic microfluidic lenses allow for real-time dynamic manipulation of the lens focal length via microfluidic injection into a PDMS membrane-capped chamber. However, limitations on current designs without surface modification preclude the use of high index of refraction silicone oils, and concave lenses. Our surface modification method of sequentially adsorbed polyelectrolytes on PDMS results in controllability of wetting characteristics for both water and silicone oil. The procedure is performed in aqueous solution, and therefore does not require line-of-sight into the enclosed lens chamber. Alternating bilayers of the polyelectrolytes: Poly(allylamine hydrochloride) (PAH) and Poly(allylamine) (PAA), successfully yielded a lens surface with contact angle with water of 15 degrees, and with silicone oil of 85 degrees. Wettability results were taken immediately following the polyelectrolytic dipping procedure, 1 day and 3 days later with no significant variations, as opposed to current modification techniques that can degrade with time. In addition to controlling wettability, we hope to improve the PDMS lens permeability by bulk modification with diphenyl cyclix. We expect the combined approach of surface polyelectrolytic adsorption and bulk diphenylization will significantly improve the microfluidic lens performance.

H6.23
Supramolecular Engineering with Macromolecules: From defined Block Copolymers to functional Nanomaterials. Ulrich S Schubert, Jean-Francois Gohy and Bas G.G. Lohmeijer; Laboratory or Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands.

The combination of supramolecular and polymer chemistry is one recent approach towards well-defined functional materials [1]. Depending on the nature of the utilized non-covalent interaction, the properties regarding reversibility, thermal stability or the photochemical behavior of the resulting polymers can be tuned. In the present approach block copolymers have been prepared in which the constituting blocks are held together by an octahedral metal complex [2]. For this purpose, terpyridine ligands have been introduced at one of the chain ends of polymers of different molecular composition and weight. The selective construction of heteroleptic bis-terpyridine complexes with ruthenium ions allows the facile preparation of metallo-supramolecular block copolymers. Detailed information regarding synthesis, purification and characterization will be shown, including electrophoresis and analytical ultracentrifugation. It also implies difficulties with standard analytical tools such as size exclusion chromatography and mass spectrometry for which solutions will be presented as well. Bulk morphology of selected block copolymers has been studied using AFM, TEM and SAXS. Amphiphilic block copolymers have been used for the preparation of metallo-supramolecular micelles [3]. Effects of temperature, pH and ionic strength have been investigated in detail and, where possible, have been compared with their covalent counterparts [4]. Last but not least, the reversibility of the metal complex is addressed as a possible and effective route for the preparation of functional nanomaterials [5]. [1] U.S. Schubert, C. Eschbaumer, Angew. Chem. Int. Ed. 2002, 41, 2892; B.G.G. Lohmeijer, U.S. Schubert, J. Polym. Sci.: Part A: Polym. Chem. 2003, 41, 1413. [2] B.G.G. Lohmeijer, U.S. Schubert, Angew. Chem. Int. Ed. 2002, 41, 3825. [3] J.-F. Gohy, B.G.G. Lohmeijer, U.S. Schubert, Macromolecules 2002, 35, 4650; J.-F. Gohy, B.G.G. Lohmeijer, S.K. Varshney, U.S. Schubert, Macromolecules 2002, 35, 7472; J.-F. Gohy, B.G.G. Lohmeijer, S.K. Varshney, B. Decamps, E. Leroy, S. Boileau, U.S. Schubert, Macromolecules 2002, 35, 7427. [4] J.-F. Gohy, B.G.G. Lohmeijer, U.S. Schubert, Macromol. Rapid Commun. 2002, 23, 555; B.G.G. Lohmeijer, U.S. Schubert, Macromol. Chem. Phys. 2003, 204, 1072; J.-F. Gohy, B.G.G. Lohmeijer, U.S. Schubert, Chem. Eur. J. 2003, 9, in press.

H6.24
SPM investigation for an electrochemical or a micro-gravimetric DNA-sensing procedure. HeaYeon Lee, JongMin Kim, JongWan Park, Hosub Jung and Tomoji Kawai; Osaka university, Osaka, Japan.

New genetic testing requires the development of easy-to-use, fast, inexpensive, miniaturized analytical chip because traditional methods for detecting DNA hybridization are slow and labor intensive. Recent reports for the direct electrical reading and/or micro-gravimetric recognition of DNA interaction offer a great promise for developing simple, rapid, low-cost and user-friendly DNA sensing devices (DNA chip). In these methods, the procedure generally relies on the immobilization of a single-stranded oligonucleotide probe onto a transducer or electrode surface to recognize its complementary target sequence. Our group is also developing an electrical-sensitive DNA chip utilizing protein-protein binding characteristics in which the proteins are modified with oligonucletide DNA. The reaction mechanism is well described by several researches but the understanding for the fabrication of this kind of the chip is still not satisfactory. In our presentation, we will show the direct surface chemical imaging for the chip surface preparation, protein-protein interaction, and complementary base recognition using atomic force microscopy (AFM) and scanning near-field optical microscopy (SNOM). We will show a highly ordered chip surface, protein-protein interaction imaging and finally DNA-sensing imaging with a few nanometer scales.

H6.25
Bioactivity of Silicon Nanowires. Dattatri K Nagesha and Jeffery L Coffer; Chemistry, Texas Christian University, Fort Worth, Texas.

In the last few years, different forms of crystalline silicon have been extensively researched for use in a variety of fields, ranging from optoelectronics to sensors to biomedical applications. The one-dimensional nature of silicon nanowires (SiNWs) is of special interest as it offers relatively well-defined large surface areas in addition to unique electronic, optical, mechanical and chemical properties due to quantum confinement. This presentation focuses on an analysis of the bioactivity of SiNWs via monitoring the in-vitro formation of calcium phosphate (the mineral phase of bone) on the surface of these nanowires. SiNWs of different diameters were synthesized using the VLS process and suitably modified to evaluate the impact of surface chemistry on calcification. The role of electrical bias on the morphology of the calcified nanostructures was also assessed. The calcification process was monitored using standard techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and infrared (IR) spectroscopy. These results suggest the possible application of these SiNWs-based systems as responsive biocompatible materials, especially in the realm of orthopaedics.

H6.26
From Biology to Bioinspired Materials: Synthesis of Silica and Germania. Siddharth Vijay Patwardhan and Stephen J. Clarson; Materials Science, University of Cincinnati, Cincinnati, Ohio.

Nanoparticles possess shape and size dependant properties that can be utilized in various applications such as semiconductors, optically active materials, sensors, etc. Methods involving the synthesis and organization of such nanoparticles or nanocrystals are thus of interest. Routes to attain the design and preparation of desirable architectures by organization of pre-synthesized nanoparticles using synthetic and biological macromolecules (such as DNA) have gained attention in recent years. Self-assembly and ionic interactions are among the key features in protein directed biomineralization. Such mechanisms can be exploited *invitro* for the synthesis and nano-patterning of various systems based on silicon, aluminum, germanium, boron, tin, silver, gold, iron, calcium and so on. Herein, we present some bioinspired strategies that can successfully synthesize nano- and microstructures. These are based upon utilizing the catalytic and structure directing roles of various (bio)macromolecules such as polypeptides derived from micro-algae, tailor-made polypeptides, polyamino acids and synthetic polymers. The formation of silica and germania structures as facilitated by such synthetic and biological macromolecules will be presented.

H6.27
Synthesis and Characterization of Very High Surface Area, Ordered Meso-porous Silica. James G Shen[1], John Catino[2], Gary Tomaino[2] and Nigel Sanders[1]; [1]R&D, Specialty Minerals Inc., Bethlehem, Pennsylvania; [2]Analytical, Minerals Technologies Inc., Easton, Pennsylvania.

Highly-ordered silica materials with uniform meso-porous structures (1.8 nm), super-high surface area (SSA, 1500 m2/g) and excellent thermal stability have been assembled by biomimetic pathways using surfactant templates as structure-directing agents. The resulting silicas exhibited framework pores of 1.8 - 3.7 nm diameter, 0.76 - 0.87

cm3/g volume and BET surface area 800 - 1500 m2/g. Synthetic variables includes pH control during the templating process. We observed that surfactant alone was less effective in directing the fabrication of silica pore in very low pH (< 0.3) conditions, resulting in the formation of nano-particles silicas. Nonionic triblock copolymers such as EOxPOyEOz are superior templates to mediate the construction of large pore (~6 nm) silica under neutral conditions. The approach demonstrated a wide range of possiblities in tailoring the structures of silicas synthesized using convenient reagents. Such meso-porous silica materials have application in large-molecule catalysis, chemical adsorption, bio-molecule separations and drug-delivery.

H6.28
Expression and Characterization of G Protein-Coupled Receptors on Nano-Sized Bacterial Magnetic Particles.
Tomoko Yoshino, Haruko Takeyama, Tsuyoshi Tanaka and Tadashi Matsunaga; Biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan.

Seven-transmembrane proteins, G protein-coupled receptors (GPCRs) play central roles in a wide range of biological processes and are prime target for drug discovery. GPCRs have large hydrophobic domains, thus the process for purification of GPCRs from the cell membrane are frequently time-consuming and typically results in loss of native conformation. In this study we assembled GPCRs on nano-sized bacterial magnetic particle (BMPs) surrounded with lipid membrane by genetic engineering using *Magnetospirillummagneticum* AMB-1. D1 dopamine receptor (D1R) was used as a model GPCR. Expression plasmid containing the fusion gene encoding D1R and Mms16, which is most abundantly produced on BMPs, was constructed and introduced into strain AMB-1. D1R-BMPs complexes were simply extracted by magnetic separation from ruptured AMB-1 transformants. After several washings, the complexes were ready to use for analysis. D1R expression was confirmed on BMPs by ELISA using anti-D1R antibody, indicating that Mms16-D1R fusion protein was assembled onto the BMP surfaces. Saturation binding analysis was used to assess the affinity of antagonist [^{3}H] SCH23390 to D1R-BMP complexes. Recombinant BMPs displayed a single affinity for the [^{3}H] SCH23390 with a Kd value of 9.7 nM. This is in good agreement with the value obtained from D1R prepared from cell membranes of Sf9 cells. For the development of a ligand screening system using D1R-BMP complexes, competitive binding assay was performed using fluorescence ligand. In the presence of bodipy-labeled SCH23390, various concentrations of dopamine were added and competitive binding assay were performed. Fluorescence of BMPs was measured after several washings. As a result, the increase of competing chemical concentrations decreased the fluorescence of BMPs. This system makes possible the convenient acquisition of the native conformation of GPCRs without the need for detergent solubilization, purification and reconstitution after cell disruption. Biomaterials produced by magnetic bacteria are powerful tools for automated applications.

H6.29
Metal Removal by Using Magnetic Bacteria. Yoshiko Okamura, Yuko Nakata, Haruko Takeyama and Tadashi Matsunaga; Biotechnology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

Magnetic bacteria synthesize intracellular magnets termed bacterial magnetic particles (BMPs) with sizes ranging from 50 - 100 nm in diameter and number over 10 per cell. BMPs are composed of magnetite (Fe_3O_4) or greigite (Fe_3S_4) with a single magnetic domain. We have previously reported the detection of endocrine disrupting chemicals with BMPs displaying estrogen receptor. In this study, we propose a metal removal method by using cell surface display on magnetic bacteria. Collection of cells is one of the major problems in microbiological bioremediation. Harvesting cells by centrifugation from bulk cultures is tedious, time consuming and costly. Since magnetic bacteria swim along magnetic filed lines and posses the innate ability to intracellularly accumulate tellurium and cadmium, they are ideal biomaterials for the magnetic separation of contaminating metals. Moreover, they exhibit tolerance to lithium, cesium, magnesium, strontium, barium, cobalt and zinc. Cell surface display in the magnetic bacterium *Magnetospirillummagneticum* AMB-1 was performed by containing recombinant *ompA* (outer membrane protein gene) or *fhuA* cloned from *E.coli*. Recombinant OmpA or FhuA were designed to display metal-affinity peptides. Metal-affinity peptides and inserted positions were evaluated by measurement of metal recovery amounts. Moreover, various metal ion species were examined with substitution the peptides.

H6.30
Nanostructured bioactive coatings by sol-gel synthesis and rapid thermal processing. LaKeisha Goins[1], Samuel Holliday[2] and Andrei Stanishevsky[3]; [1]Talladega College, Talladega, Alabama; [2]University of Alabama at Birmingham, Birmingham, Alabama; [3]Physics, University of Alabama at Birmingham, Birmingham, Alabama.

Bioactive calcium-based coatings like hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and recently $CaTiO_3$ are of great interest for application in biomedical implants. Several coating parameters such as composition, crystalline grain size, and surface morphology play crucial role in this application field. The nature of the substrate implant material, for example, titanium and its alloys, is also an important factor affecting the coating adhesion to the substrate, and mechanical strength of the system. It has been observed that nanocrystalline hydroxyapatite coatings demonstrate better bioactivity than a coarse-grained material, or biomedical titanium alloys. We present the results of an investigation of sol-gel deposition of nanostructured hydroxyapatite (HA) and $CaTiO_3$ coating systems onto nanocrystalline thin-film substrates including Ti and TiO_2 (both rutile and anatase modifications). Hydroxyapatite coatings were also prepared on $CaTiO_3$ layer. The calcium - phosphorus and calcium - titanium precursors were spun onto the substrates at 2000 - 4000 rpm. A 30-50 nm thick layer was formed after each coating cycle. The 200 - 500 nm thick nanocrystalline coatings were formed by repeating the coating procedure several times followed by rapid thermal processing (RTP) in oxygen or nitrogen. Several multilayer systems of (HA-$CaTiO_3$)n and (HA - TiO_2)n were also prepared to study the interaction between the layers during the thermal processing. Crystallization of single phase $CaTiO_3$ was observed at 600°C, and nanocrystalline HA was observed at 800°C after RTP for 2 minutes. The effect of sintering ambient during the rapid thermal processing on the crystallization process was studied. The formation of the $CaTiO_3$ interface layer was observed during RTP of HA coating on Ti and TiO_2 substrates, as well as in HA - TiO_2 multilayer system. We discuss in detail the influence of the substrate material and the effect of thermal annealing procedure on the structure and properties of studied materials. We acknowledge support from the National Science Foundation, Research Experiences for Undergraduates (REU)-Site award to the University of Alabama at Birmingham (UAB) under Grant No. DMR-0243640.

H6.31
Tuning Crystal Nucleation and Growth Using Self-Assembled Monolayers. Yong-Jin Han and Joanna Aizenberg; Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

Control over the nucleation and growth of biologically formed crystals is truly remarkable. We have utilized self-assembled monolayers (SAMs) to understand the principles controlling the formation of calcium carbonates, including their crystallographic orientation, morphology and size. By selectively choosing the SAMs and introducing specialized additives during the growth of these crystals (e.g. Mg ions), we were able to exert the multi-level control of the formation of calcium carbonate. In order to elucidate the mechanisms of the oriented nucleation, morphological modification and size control, detailed studies of the correlation of the structures of SAMs and crystals they nucleate, as well as of the effect of the additive concentration was performed. We believe that understanding the formation of biominerals will lead to many practical applications.

H6.32
Photoluminescence of a Conjugated Polymer-Polyelectrolyte Assembly and Effective Quenching in Aqueous Solution and on Self-Assembled Thin Film Architectures.
Gabriel Alonzo Montano, Andrew M Dattelbaum, Jim H Werner, Wenguang Li, Hsing-Lin Wang and Andrew P Shreve; Bioscience Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Control of assemblies driven by polyelectrolyte interactions represents a biologically inspired approach to materials synthesis. One means of investigating such assemblies is through photoluminescence spectroscopy of luminescent polyelectrolytes. A photoresponsive assembly was formed in aqueous solution between poly (2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) and DAB-Am-16, a generation 3.0 polypropylenimine hexadecamine dendrimer (DAB). The photoluminescence(PL) intensity from an aqueous solution of MPS-PPV was greatly enhanced upon addition of DAB and found to increase, as well as red-shift, with additional DAB. Efficient quenching of MPS-PPV photoluminescence has also been observed by using sulfonated-C60 in aqueous solution and self-assembled on thin film architectures. These results provide a greater understanding of the photoluminescence from polyelectrolyte assemblies and indicate possible uses in high-sensitivity chemical and biological sensing and in light-emitting displays (LEDs).

H6.33
Synthetic Melanin Thin Films: Surface Structure and Electrical Properties. Maria Ivonete Nogueira da Silva[1], Gabriela Simone Lorite[1], Shirlei N Deziderio[2], Juan Carlos Gonzalez[3], Carlos

FO Graeff[2] and Monica Alonso Cotta[1]; [1]IFGW - DFA, UNICAMP, Campinas, SP, Brazil; [2]FFCLRP, USP, Ribeirao Preto, SP, Brazil; [3]LNLS, Campinas, SP, Brazil.

Melanins are important pigments found in many organisms and tissues. They have attracted great attention due to their role in photoprotection and technological applications as ultra-violet light filters, for example. In this work we will study the effect of hydration on the local structural and electrical properties of synthetic melanin thin films. Melanin powders synthesized from L-dopa using either DMSO (Dimethyl Sulfoxide) or pure water were prepared. Synthetic melanin thin films (about 100nm thick) were prepared by evaporating (casting) solutions of these powders on crystalline silicon substrates. After dried out, some of the samples were hydrated in a humid chamber. The samples were analyzed using Atomic Force Microscopy (AFM), Electrical Force Gradient Microscopy (EFM), and Conductive Atomic Force Microscopy (C-AFM). TappingMode ultra sharp Si tips were used for AFM and EFM measurements. C-AFM was carried out with a Au/Cr coated Si tip (estimated radius of 40nm). The film morphologies were studied with AFM. Samples prepared with DMSO presented a continuous film, with good adhesion to the substrate, while more inhomogeneous films were obtained for water-prepared samples. Extended flat terraces with small round depressions were observed for the DMSO samples. The samples prepared in water, however, exhibited a rougher surface, with larger microstructures. The hydrated DMSO-prepared melanin samples exhibit large agglomerates in the center of the depressions with heights in the range 1 to 3 nm. For the non-hydrated sample, the agglomerates are rarely present at the initial surface but their density has been observed to increase slowly in time when the sample is kept at ambient conditions. Roughness exponents of the surfaces, both on the planar and agglomerate regions, were calculated. The planar regions provide similar exponents for both the hydrated and non-hydrated samples, indicating that this process does not affect the surface microstructure which was most likely formed in the solution. However, the agglomerates present larger roughness values, closer to those observed for the water-prepared samples. EFM and C-AFM were used to study the electrical properties of the samples in correlation with their morphology. An increment of the EFM signal was observed for both samples at the edges of the flat terraces. However, a lower EFM signal was found in the agglomerates. The decrease of the EFM signal indicates a lower free radical density produced by hydration of the sample. This is indeed confirmed by C-AFM data which shows different resistivities in the agglomerate regions. Our results suggest that the thin film is formed by relatively large planar structures which are subsequently deposited onto the silicon surface. The agglomerates originate from reaction with water at specific locations on the surface, most likely defects on the planar structure.

H6.34
Shape Adaptable Water-soluble Conjugated Polymers. bin liu, Shu Wang, Guillermo C Bazan and Alexander Mikhilovsky; Dept of Chemistry & Materials, Institute for Polymers and Organic Solids, Univ. of california, Santa Barbara, Santa Barbara, California.

Conjugated polymers provide highly responsive optical platforms for chemical and biological detection. Water-soluble conjugated polymers are of particular interest for reporting biological recognition events. Cationic conjugated polymers such as poly(9,9-bis(6'-N,N,N-trimethylammonium)hexyl)-fluorene phenylene) form part of a DNA-sensor technique which utilize both the optical amplification of conjugated polymer and the complexation of polyelectrolytes with opposite charges. In this contribution we report on a synthetic method for producing cationic conjugated polymers with a range of backbone regiochemistries. We show that, despite structural differences which affect the average conjugation length, there is facile energy transfer amongst polymer segments and similar emission properties and FRET function. Additionally, the non-linear cationic conjugated polymers are more efficient excitation donors.

H6.35
Nano-Scale Roughness Inducing Super-Water-Repellency: From Natural to Artificial. Yunying Wu[1,2], Changsong Liu[1], Masao Kouno[3], Hiroyuki Sugimura[3], Yasushi Inoue[4] and Osamu Takai[1]; [1]Takai, Center for Integrated Research in Science and Engineering, Nagoya University, Nagoya 464-8603, Japan; [2]Aichi Science & Technology Foundation, Nagoya 460-0002, Japan; [3]Department of Materials Processing Engineering, Nagoya University, Nagoya 464-8603, Japan; [4]Research Center for Nuclear Materials Recycle, Nagoya University, Nagoya 464-8603, Japan.

Previous studies showed that both micro- and nanoscale hierarchical surface structures (like lotus leaves - branch-like nanostructures on top of the micropapillae) were the key to produce super-hydrophobicity. The height of asperity was less important than asperity shape in determining wetting by theoretical calculation and experiment. However, the present work on some plant leaves reveals that the super-hydrophobic property is mainly affected by these nanostructure although the surface of these leaves consists of both nano- and microstructures. In addition, the hydrophobic property is independent on the shapes of nano-scale asperities. The results from the natural world provide a guide for constructing artificial super-hydrophobic surfaces with nano-scale fine roughness by using microwave plasma-enhanced chemical vapor deposition (MWPE-CVD) and focused ion beam (FIB) forming. The water contact angle of such artificial surface is mainly affected by the asperity height. This would be the results of more air trapped in the pores between higher height asperity if the fine-rough surface was made up of nano- (or submicro-)scale feature. This work is supported by JSPS - RFTF99R13101 and ASTF.

H6.36
Inositol Phospholipids as Novel Agents for Controlling Intracellular Trafficking. Andrew B Holmes, Stuart J Conway, Melloney K Johns and Christoph Meyer; Chemistry, University of Cambridge, Cambridge, United Kingdom.

Phosphatidyl inositol polyphosphates (PIPs) have emerged as a powerful tool for probing the downstream processes which control intracellular signalling. This paper reports the novel synthesis of simple lipid analogs of many known and novel PIPs and their use to identify many new proteins involved in signal transduction. For example attachment through the lipid side chain to affinity columns provides a powerful new tool in therapeutic applications for a wide variety of disease states. Even phosphatidic acids are found to bind to important proteins associated with housekeeping and coatamer processes. New results with photo-cleavable phospholipids will be reported.

H6.37
Icosahedral Virus: Assemblies toward photonic crystals. Shane Juhl[1], Lynn Waterhouse[1], Ryan Kramer[1], Richard Vaia[1], Sam Ha[2], Edwin Chan[2], Edwin Thomas[2], James Kalmakoff[3] and Vernon Ward[3]; [1]AFRL/MLBP, Wright-Patterson AFB, Ohio; [2]MIT, Boston, Massachusetts; [3]University of Otago, Otago, New Zealand.

Natural systems present many opportunities for the advancement of optical materials due to the large number of naturally occurring self-assembled structures that are theoretically predicted to exhibit unique photonic properties. In contrast to the homogeneous surface of its non-biological counterpart, polymer colloids, the heterogeneous surface chemistry of the icosahedral protein capsid of virus particles offers a myriad of opportunities to realize non-closed-packed structures. The Chilo and Wiseana Iridovirus are grown in waxmoth larvae and are collected through filtration and centrifugation. The iridovirus was used to demonstrate bottom-up assemblies of virus particles that exhibit optical reflection in the visible regime. Assembly methodologies investigated include centrifugation, capillary flow, crystallization, flow field, sedimentation, and dielectrophoresis. Bulk virus assemblies exhibit non-closed-packed structures, whereas the initial one to three layers near a surface exhibit closed-packed arrangement. The lower surface charge of the virus and topological features of the caspid imply that the relative assembly of the particles is sensitive to pair-wise orientation of the icosahedra as well as concentration and pH changes. This contrasts polymer colloids, whose spherically symmetric interaction potiential and higher surface charge dominates the inter-particle forces between the colloids restricting the accessible packing geometries.

H6.38
Engineering viruses for colloidal self-assembly. Kirstin Purdy and Seth Fraden; Physics Department, Brandeis University, Waltham, Massachusetts.

Suspensions of colloidal rods self assemble into isotropic, nematic, cholesteric and smectic liquid crystal phases. We study the charged rodlike virus fd whose interparticle interactions are dominated by electrostatics. With increasing solution ionic strength the range of the electrostatic interactions is decreased. By coating the viral surface with functionalized neutral polymers larger in size than the range of electrostatic interactions, we create colloidal rods that interact solely through steric polymer-polymer interactions. By selectively binding to specific sites on the viral surface with these functionalized polymers one of our goals is to create virus-polymer block copolymers. We study the phase behavior of these virus-polymer colloids in solution to quantify the role of shape and interparticle potential in the stability of liquid crystalline phases.

H6.39
Energy transfer between bio-assembled nanocrystal quantum dots. Sohee Jeong, Mark Achermann, Laurent Balet, Victor I Klimov and Jennifer A Hollingsworth; LANL, Los Alamos, New Mexico.

The ability to construct ordered two- and three-dimensional

structures on the nanometer scale is essential for the development of next-generation optical, electronic, and magnetic materials and devices. We utilize motor protein and microtubule systems, which nature has evolved to transport cargo at the nanoscale in an energy-dependent manner, for assembly of artificial nanostructures. Here, semiconductor nanocrystal quantum dots (NQDs) comprise the cargo. At the same time, NQDs are robust and optically tunable fluorophores, making them ideal candidates for such applications as fluorescent markers in biological imaging. We prepare high quality (in terms of optical properties and size dispersion) NQDs coated with hydrophobic organic ligands and subsequently incorporate them into functionalized lipid-based micelles, thereby permitting water solubility and conjugation to target biomolecules. We study assembly of different-sized, micelle-encapsulated NQDs by observing inter-particle energy transfer as NQDs are brought into and out of close proximity with one another. Energy transfer provides a useful and sensitive tool for monitoring active bioassembly of NQDs.

H6.40

Bio-Inspired One-Pot Synthesis of Magnetic Nanomaterials. Carlos B. W. Garcia[1], Anurag Jain[1], Surbhi Mahajan[1], Yuanming Zhang[1], Francis DiSalvo[2] and Ulrich Wiesner[1]; [1]Materials Science and Engineering, Cornell University, Ithaca, New York; [2]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Biological systems have undergone long evolutionary optimization processes using macromolecules to structure inorganic material to form their skeletal parts. These include the formation of amorphous (radiolarian), polycrystalline (bone and teeth), and single crystalline type materials. Each of these approaches provides inspiration for the design and construction of technologically important materials. Borrowing from the first two concepts, we have observed the formation of crystalline ferric oxide in an amorphous aluminosilicate matrix nanostructured with a block copolymer leading to multifunctional materials. Block copolymer-ceramic nanocomposite films were cast through an evaporation induced self-assembly (EISA) approach from a one-pot solution containing iron-aluminosilicate sol-gel precursors and poly(isoprene-block-ethylene oxide). This simple pathway leads to superparamagnetic mesoporous materials and nanoparticles with potential applications in magnetic separation, molecular labeling, and catalysis technologies. Nanoparticles in the shape of spheres, cylinders, and plates were generated from the sphere, hexagonal cylinder, and lamellar reverse mesophases, respectively, by dissolution of the polymer matrix with a selective solvent. Mesoporous materials were formed by pyrolysis of the polymer channels of the inverse hexagonal cylinder and cubic bicontinuous regular mesophases. Calcination of the materials nucleates and grows magnetic ferric oxide particles within the aluminosilicate matrix. Transmission electron microscopy and magnetic properties characterization using a SQUID magnetometer reveal the approximate size of the ferric oxide particles is 5 nm. The approach eliminates the possibility of clogging the pore structure in the mesoporous materials as observed in back filled systems.

H6.41

Noncovalent Immobilization of wild type Phosphotriesterase in Polyelectrolyte Multilayers. Yongwoo Lee and Alok Singh; Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington, District of Columbia.

Wild type phosphotriesterase (PTE) catalyzes the hydrolytic degradation of organophosphates. In order to physically stabilize and sustain its activity, PTE were sandwiched between polyelectrolyte layers of opposite charges and held in layers through electrostatic interaction without distorting the enzyme architecture. Silica microspheres (30-50μ in diameter) were used as support for polyelectrolyte layers and the microspheres were evaluated for their catalytic activity in varying humidity environment. Thus, polyelectrolyte layers made from branched (polyethyleneimine) (BPEI) were used for embedding PTE and poly(acrylic acid) (PAA) was used for capping the multilayers after constructing five PTE layers. Enzyme and polyelectrolyte deposition was confirmed by employing quartz crystal microbalance (QCM) to demonstrate the stepwise growth of layers under the conditions used in the case of silica microspheres. Enzymatic activity of PTE immobilized was measured as the amounts of p-NP produced from hydrolysis of methyl parathion (MPT). PTE bearing glass beads showed sustained enzymatic activity against a pesticide methyl parathion (MPT) after stored at 25 °C for more than 100 days. The reusability of the PTE beads against MPT was demonstrated by carrying out multiple hydrolysis cycles. Beads also displayed sustained activity under high humidity environment for a period of weeks indicating that enzyme immobilization involving electrostatic attraction is a viable means in building bioactive coating(s). In-situ formation of a polymer net by water soluble, polymerizable molecules, TMSED and N,N-bis (methacryloyl)-4-aminophthalic acid, on the outermost polyelectrolyte layer through charge-neutralization rendered robust multilayer assemblies. These assemblies were functional in high salt concentration, which is known to exert stress and delaminate layers.

H6.42

Super-Hydrophobic Thin Films for Organic Molecular Adsorption. Yunying Wu[1,2], Megumi Iyoshi[3], Hiroyuki Sugimura[3], Changsong Liu[1], Yasushi Inoue[4], Osamu Takai[1] and Shigeru Kurosawa[5]; [1]Takai, Center for Integrated Research in Science and Engineering, Nagoya University, Nagoya 464-8603, Japan; [2]Aichi Science & Technology Foundation, Naka-ku, Nagoya 460-0002, Japan; [3]Department of Materials Processing Engineering, Nagoya University, Nagoya 464-8603, Japan; [4]Research Center for Nuclear Materials, Nagoya University, Nagoya 464-8603, Japan; [5]National Institute of Advanced Industrial Science and Technology, 1-1 Higashi, Tsukuba 305-8561, Japan.

Various phenomena, such as snow sticking, contamination or oxidation, and current conduction, are expected to inhibit on a super-hydrophobic surface. Here we report organic molecular adsorption on such surface. The film, deposited onto a quartz crystal microbalance (QCM) sensor, was prepared by microwave plasma chemical vapor deposition (CVD), using trimethylmethoxysilane as raw materials and Ar as additive gas. Such film has a proper nanotexture and a hydrophobic surface terminated with methyl groups, which consequently showed ultra water-repellency. Then we evaluated the amount of organic molecules adsorption by examining resonance frequency, which is sensitive to the mass change. The results showed that organic materials (vapor), such as formaldehyde, methanol, ethanol, acetone, toluene and hexane, preferentially adsorbed on the film, while the adsorption of water vapor was restricted due to the hydrophobic nature of the surface. The amount of the adsorbed organic molecules seemed to depend on the molecular polarity because of a prefer adsorption for some organic molecules with less polarity. The nanotexture of the film was crucial to increase the organic molecular adsorption amount through the effective surface areas increasing. The selective organic molecular adsorption properties are expected to serve as environmental materials (i.e. sensor, sorbent) to detect (or adsorb) toxic organic gas. This work is supported by JSPS - RFTF99R13101 and ASTF.

H6.43

Competitive Adsorption at the Air-Water Interface From a Self-Assembling Polymer-Surfactant Mixture. Young-Soo Seo[1], Krishnan Chari[2] and sushil Satija[1]; [1]NCNR, NIST, Gaithersburg, Maryland; [2]Kodak, Rochester, New York.

A mixture of polymer and surfactant is frequently used in the preparation of colloidal dispersions and emulsions. Typically, the surfactant is needed for reducing interfacial energy whereas the polymer is needed for imparting stability against Brownian coagulation, coalescence, Ostwald ripening or crystal growth. The effectiveness of a polymer-surfactant mixture is dependent on the interplay between self-assembly in the bulk fluid and adsorption at the interface. Here we study this relationship using the air-water interface as a model for more complex colloid-water or emulsion-water interfaces. We demonstrate using a combination of neutron reflectivity and surface tension measurements that polymer-surfactant assembly in bulk water enables co-existence of polymer and surfactant at the interface via partial displacement of adsorbed surfactant by the polymer. The latter is extremely important in colloidal stabilization. It is widely recognized that surfactant can displace polymer at high enough concentrations but not vice versa.

H6.44

Self-Propagating High-Temperature Synthesis of Porous Nickel-Titanium for Bone Engineering Applications. D L Belk[1,2], R A Ayers[1] and J J Moore[2,1]; [1]Center for Commercial Applications of Combustion in Space, Colorado School of Mines, Golden, Colorado; [2]Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado.

Porous Nickel-Titanium (NiTi) is a strong candidate material for bone engineering applications because its mechanical properties are within the range of bone and its porosity allows for biologic interlock of the material to the surrounding tissue. Self-propagating high-temperature synthesis (SHS) is one method for producing porous NiTi. Nickel and titanium powders, -325 mesh, were mixed for 24 hours then pressed into cylindrical pellets (0.5 inch diameter, 0.5 inch height) to a theoretical green density of approximately 53%. The pellets were preheated in flowing argon for one hour then ignited using a tungsten coil. Scanning electron microscopy and electron dispersive spectroscopy show localized differences of stoichiometry suggesting variations in the crystal structure where the Ni to Ti atomic ratio varied between 48.5:51.5 and 50.7:49.3. X-ray diffraction (Philips X'Pert PRO) confirmed the presence crystalline equiatomic NiTi as well as other intermetallic compounds including $NiTi_2$ and Ni_4Ti_3 .

Nanoindentation (MTS Nano Indenter XP) of this heterogeneous material indicates a mean range indentation modulus of 89.6 ± 9.4 GPa. This is on the same order of magnitude as bone, which has an elastic modulus range of 14-20 GPa. Ongoing work is examining the effect of green density, combustion temperature and preheat to control NiTi stoichiometry, porosity, and microstructure to optimize this material for bone engineering purposes. It is anticipated that increasing porosity and/or reducing the presence of other intermetallic components will result in a more appropriate mechanical match between the NiTi and bone tissue.

H6.45

Quantitative Analysis on DNA-Grafting Densities for the Assembly of 2-D Opaline Arrays. Sejong Kim[1], Erik Geiss[2], Harris L. Marcus[2] and Fotios Papadimitrakopoulos[1]; [1]Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut; [2]Department of Metallurgy and Materials Engineering, Institute of Materials Science, University of Connecticut, Storrs, Connecticut.

Recently, DNA hybridization has been increasingly adopted in materials sciences due to its capability of specific and reversible molecular recognition. These unique properties of DNA have been used for the realization of 2-D assembly of colloidal particles as a precursor to constructing 3-D photonic crystal in a layer-by-layer manner. In order to precisely understand this DNA-assisted assembly of colloidal particles, in this study, we quantitatively assessed the surface density of grafted and hybridizing accessible DNA oligomers on both substrate and colloidal particles. The DNA grafting densities were determined by UV-VIS of dye-functionalized complementary DNA oligomers, in conjunction with theoretical models. The variations of the concentration of hybridized DNA as a function of parameters such as the number of DNA base pairs, the length of spacer and the size of particle were also investigated to determine the immobilization strength of colloidal particles on various surfaces.

H6.46

Cell Growth on Prestructured Microelectronic Semiconductor Materials. Heinz D Wanzenboeck[1], Christian Almeder[1], Christoph Pacher[1], Emmerich Bertagnolli[1], Michael Wirth[2] and Franz Gabor[2]; [1]Institute for Solid State Electronics, Vienna University of Technology, Vienna, Austria; [2]Institute for Pharmaceutical Technology and Biopharmacy, University Vienna, Vienna, Austria.

The rapid advance of semiconductor technology has resulted in a size revolution of microelectronic devices. Feature sizes below 200 nm have become standard in many microchips such as DRAMs. The devices fabricated in semiconductor technology can be produced a magnitude smaller than biological units and hence provide the potential for novel in-vivo sensors, actuators or novel analysis and data collection approaches. The interface between microelectronics and biomaterials serves a central role in future engineering of biomedical sensors and functional devices. This study focuses on the material science aspects of the cell-semiconductor interface. The toxicity of materials used in microelectronics for human cells was investigated. Tissue cultures were grown on silicon, silicon oxide, several organic and inorganic dielectrics and a representative selection of metals. Human colon carcinoma cells (Caco-2) were used as exemplary cell line to test the biocompatibility of materials. CaCo-2 cells are a widely used in vitro model for studies and are robust under environmental stress. The Caco-2 cells were cultured on semiconductor chips stored in polycarbonate culture plates. The samples were incubated at 37°C for a period of 10-14 days. The growth rate, the cell coverage of the surface after a defined growth time and the cell adhesion were investigated. Results were compared to the growth progress on standard glass slides. Preliminary results showed a well-behaved growth of cells on Au and Si3N4. Patterned substrates of thin Au lines on Si3N4 dielectric layers were also used as support substrate for cells. The grown Caco-2 cells displayed a good adhesion to the substrate. These initial experiments opened the gate to functionalized materials for bioelectronics. Further studies are required to provide the necessary multidisciplinary environment that thoroughly links biology, nanoengineering, and medicine. Potential applications involving cellular processes either in vitro or in vivo will be discussed.