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Symposium C: Bio-inspired Nanoscale Hybrid Systems

Objectives, Highlights

Symposium C, Bio-Inspired Nanoscale Hybrid Systems, provided an extensive overview of the new and advanced approach to synthesize functional materials and to fabricate nanoscale devices utilizing biomolecules as a key building block.

Nature utilizes molecular recognition between complex biomacromolecules to form sophisticated meso- and macroscopic architectures with tremendous control over the placement and orientation of nanoscopic building blocks. On the other hand, the advances of nanotechnology provide us new nanoscale structures including nanoparticles, nanowires, nanofabricated circuits etc. The marriage between biomolecules and these new nanostructructures allows us to envision many scientific breakthroughs and commercial applications.

For example, specific interactions between biomolecules can be utilized as a major driving force to build sophisticated 1D, 2D and 3D architectures. C. A. Mirkin (Northwestern Univ.) demonstrated "biodirected synthesis of functional materials using nanoscale building blocks" where biomolecular interactions such as DNA hybridization is utilized to direct the assembly of nanoparticles to form desired architectures. Several researchers reported various bio-inspired synthesis and assembly results such as the synthesis of metallic nanowires from peptides, DNA-mediated assembly of carbon nanotubes, and 3D assembly of nanoparticles using virus as a template.

New advanced characterization tools are applied for the quick and high precision analysis of bio-inspired hybrid nanostructures. H. Fuchs (University of Munster) presented "advanced dynamic scanning probes for the characterization of self-organized organic layers." Electron transport properties of hybrid nanostructures are studied via conducting atomic force microscope or electrode junctions by several researchers. On the other hand, conventional fluorescence microscope, scanning electron microscope, and transmission electron microscopes are optimized for hybrid nanostructures providing valuable information to understand these new nanoscale systems.

Bio-inspired hybrid nanostructures results in new commercial applications. P. Alivisatos (UC Berkeley) applied functionalized "nanocrystals for biological applications" including ultra-sensitive biomolecular detection schemes. M. Zheng (DuPont) presented "bioassembly of nanometerials for nanoelectronics" where bio-inspired hybrid nanostructures are utilized as an electronic component. Functionalization of solid surfaces with biomolecules is also becoming increasingly important because of its possible bioengineering applications such as bio-compatible solid surface development, cell adhesion and growth on solid surface, the development of artificial bone graft substitute etc.

Selected, important Presentations

ARRAYS, ESSAYS, DIAGNOSTICS

Biomaterial-Nanoparticle Hybrid Systems for Bioelectronics. (C1.2)

I. Willner presented the integration of functionalized nanoparticles and nanotubes with biomaterials for bioelectronic applications. He presented the possibilities of constructing complex structures consisting of DNA/carbon nanotubes/nanoparticles.

Willner studied the reconstitution of apo-redox-enzymes on functionalized Au-nanoparticles and carbon nanotubes. These structures associated with electrodes supports yield electrically contacted protein assemblies. He discussed the effectiveness of the electronic coupling between the redox center of the proteins and the electrode in terms of the structural features of the different nanoassemblies.

Furthermore, Willner presented the functionalization of CdS nanoparticles with nucleic acids and the incorporation of functionalized Au-nanoparticles into double-stranded DNA.

DNA-Mediated Assembly of Carbon Nanotube Devices. (C1.5)

The group of K. A. Williams developed a technique for using DNA as a means for assembling carbon nanotubes devices. They demonstrated attachment of peptide nucleic acid to single carbon nanotubes. The resulting macromolecules combine the electronic properties of nanotubes with the sequence specific recognition of DNA.

High Performance Cell Patterning for Cell-Based Sensor Applications. (C1.7)

M. Veiseh and its group used lithography and surface engineering to develop cell-patterned substrates for cell-based biosensors. The used technique is able to pattern highly selective and non-denatured proteins that retain their bioactivity and guide natural and uniform cell growth. This is a key factor of these biosensors.

Micropatterns of Au are fabricated on 2D Si surfaces by photolithography. Mixed-COOH-terminated self-assembled monolayers (SAMs) are bound to gold regions to conduct covalent immobilization of fibronectin. The patterns preferentially immobilize (or repel) proteins or peptides in desired regions, thus guiding growth of cells on the surface.

Fabrications of Peptide Nanotubes Functionalized with Biological and Molecular Recognitions and Their Assemblies into Device Configurations. (C2.1)

H. Matsui and his group have fabricated peptide-based nanotubes and functionalized them with biological recognition and a host-guest molecular recognition. They used those functionalized peptide nanotubes, which can recognize and selectively

immobilized on well-defined region on the patterned substrates using protein-protein interactions. Moreover, they assembled the peptide nanotubes as nanometer-sized building blocks into device configurations, decorating them with various materials such as metals and quantum dots for electronics and sensor applications.

A New Protein Patterning Technique and its Application in Bio-Inspired Sel-Assembly. (C2.4)

D. Guo and coworkers presented a new protein patterning technique based on microelectronic fabrication, DNA hybridization and biotin-streptavidin pair.

A gold-on-silicon-dioxide substrate with micron size pattern was fabricated with photolithography. Thiol derivatized single stranded DNA was attached to the gold pattern surface by the chemical bonding between gold atom and sulfur atom. Surface attached DNA was then hybridized with a biotin conjugated complementary DNA sequence.

The authors demonstrated that this technique was used successfully in the self-assembly of 20 nm streptavidin conjugated gold particles.

Specific Interaction between a Protein and Carbon Nanotubes-Towards Biosensors. (C2.5)

In this work of C. Salvador-Morales and co-workers studied the use of functionalized carbon nanotubes as transducers in bio-sensing applications.

They investigated the interactions of several proteins with single walled and multi walled carbon nanotubes. Selective interaction of some proteins with nanotubes was achieved through fictionalization. They found that using non-covalent fictionalization of carbon nanotubes it is possible to induce specific interaction between carbon nanotubes and proteins such as Biliverdin Ixb reductase (BVRB).

Using Raman spectroscopy they found that the hydrophilic surface of BVRB protein interacts specifically with the hydrophilic surface of functionalized carbon nanotubes. Activity investigations showed that BVRB remains bioactive in the hybrid system.

Biotemplate-Directed 2-Dimensional Nanostructure Assembly. (C3.4)

S. M. Yu and coworkers applied biologically assembled nanoscale template to direct formation of 2D nanocrystal arrays. They explored purple membrane, a naturally membrane protein crystal patch from halobacteria, as a precisely structured nanometer-scale template.

They developed genetically engineered purple membranes that display unique functional groups (e. g. cystein or histidine) on the membrane surfaces with defined nanoscale symmetry. These reactive functional groups were used as specific anchoring sites for nanocrystals immobilization. The crystal patches were used to react with functionalized gold nanoclusters.

Fabrication and Application of Protein Crystal Microarrays: Demonstration of Laser Manipulation and Patterning of Protein Crystal. (C3.5)

Y. Hosokawa and coworkers presented fabrication of protein crystal micro-arrays. This preparation is very difficult in comparison with DNA micro-arrays because of complex structures of proteins.

They used a laser trapping technique to manipulate and pattern protein crystals of polyhedra. These crystals of a few _m were fixed one by one on a slide glass by laser manipulation technique. Each polyhedra crystals was trapped by local heating due to UV laser irradiation. On the trapped polyhedra, femtosecond laser was irradiated to fix it on a polymer substrate.

Protein/Polymer Hybrids as Biomimetic Valves. (C4.4)

The group of C. Montemagno presented a recent work in engineering hybrid protein/polymer systems as biomimetic valves. Pore proteins are nanometer-sized pumps and valves, transporting ions and molecules. Some of these proteins actuate in response to an applied voltages.

They genetically engineered a voltage-gatable pore protein and inserted it into monolayer planar membranes of amphiphilic block copolymers. The results of electrical and analyte transport experiments demonstrated the gating ability.

MINERALIZATION, IMPLANTS, AND SURFACES

Nano-Scale Modification of Metal Surfaces for Biomedical Applications. (C5.4)

A. M. Lipski and coworkers developed a new method for nano-scale modification of metal surfaces that facilitates the attachment of biological species, such as peptides. This technique produces surfaces with very high concentration of reactive groups on the surface. It is applicable at room temperature, has excellent reproducibility and cell compatibility.

This is very useful for improving the efficiency of metallic medical devices.

Nanostructuring of Surfaces Using Anodic Alumina Membranes-Methods, Materials and Properties. (C6.1)

T. Sawitowski presented an interesting method for nanostructuring surfaces in the nanometer scale based on the use of anodic alumina membranes. He uses nanoporous alumina as a mask to nanostructure different materials like polymers, metals or sol-gel-coatings.

This method is fast and easy compared to the sophisticated lithographic methods.

Nanostructured and Auto-Regeneration Hybrid Inorganic/Polymer Coatings for a Durable Self-Clean Effect in Optical Quality. (C6.2)

The authors presented a coating technology that provides the self-cleaning functionality in optical quality and with a long lifetime. The coating system consists of inorganic protective coating with an underlying polymeric layer. This layer contains a surfactant in a polymer matrix, which diffuses to the surface of the inorganic film and provides a hydrophobic surface. Due to the continuous self-regeneration of the surface chemistry by self-assembly and diffusion of the surfactant, a much longer lifetime can be obtained as compared to the current technology.

Synthesis of Novel Organosilicate Nanoparticles and Their Effects on Osteoblast Behavior. (C6.3)

The authors synthesized new organosilicate nanoparticles by means of low-temperature sol-gel techniques. Thanks to the flexible surface chemistry of silicates, these particles can be easily functionalized with various organic groups.

These organosilicate nanoparticles can be used in orthopedic medicine for their ability to bond to bone. They can substitute the Bioglass that have been limited in their clinical applications due to high-temperature processing conditions and low mechanical strength.

BIOMATERIALS

Advanced Dynamic Scanning Probes for the Characterizatioin of Self-Organized Organic Layers. (C7.1)
(H.Fuchs, Univ. Muenster, Germany)

H. Fuchs presented recent progress in dynamic force microscopy/spectroscopy (SFM/SFS) applied to polymers and molecular layers (OMBE- and LB films).

He showed that by using a combined experimental and computer simulation technique it is possible reconstruct force/distance curves without using any model potentials and parameters. This method permits to extract material parameters such as atomic densities of the investigated surface and the local elastic properties. Energy dissipation occurring during high-resolution imaging can also be evaluated.
Soft organic materials such as organic layers and biological systems can be imaged without deterioration.

Recent development of a novel Scanning Near Field Optical Microscopy (SNOM) technique based on an aperture less probe exhibiting a lateral optical resolution of 1-10 nm was also reported.

Molecular Biomimetics: New Strategies in Molecularly Hybrid Materials. (C7.3)

D. Heidel and coworkers used combinatorial biological techniques to select specific short polypeptides with high affinity to bind to inorganic surfaces, in particular, noble metals and semiconducting oxides.

They demonstrated that genetically engineered proteins for inorganic (GEPI) can be used as molecular erector sets to assemble nanoparticles and to create biocompatible surfaces.

Bio-Inspired Nanoscale Polymer-Ceramic Hybrid Systems. (C8.2)

U. Wiesner presented the synthesis and characterization of amphiphilic polymer based functional polymer-ceramic hybrid materials. By using appropriate functional polymers as well as ceramic precursors, he obtained a strong morphology control on the nanoscale.

The hydrophilic parts of the polymer are completely integrated into the ceramic phase like in biological hybrid materials. Through this unique polymer-ceramic interface, the ceramic phase is plasticized by the polymers thus leading to a novel class of materials referred to as flexible ceramics .

A particularly fascinating structure was discovered. It is a bicontinuous cubic morphology referred to as the Plumber s Nightmare . This structure was known from surfactant studies but was not known to exist for polymers.

PARTICLES

Biological Applications of Nanocrystals. (C9.1)

Very interesting is the work of P. Alivisatos (C 9.1) on the chemical synthesis of inorganic nanocrystals with well-defined characteristics, such as size, shape and structure. In particular, he showed that by changing surfactant mixture composition it is possible produce semiconductor, metal, and oxide nanocrystals with well-defined shapes (rod and disk). Therefore, the surfactant mixture can be used to control the growth rates of different facets of the nanocrystals, allowing a wide tunability of shape. He illustrated work involving CdSe and Co nanocrystals and transition metal oxides. The nanorods can be aligned in a variety of ways.

Some biological applications of these nanocrystals were also presented, in particular advances on DNA conjugation and assembly.

Structural, Thermodynamic and Optical Properties of DNA-Linked Metal Nanoparticle Aggregates and Arrays: Theoretical Studies. (C10.1)

G. Shatz presented theoretical studies on two surprising properties of DNA linked to Au and Ag nanoparticles.

The first property is concerned with the sharp melting transitions. The theory attributes this to multiple DNA s linking the nanoparticles, in combination with enhanced counterion condensation due to the high density of oligonucleotides.

The second concerns the recent observation of blue shift of plasmon resonance spectra for nanoparticles separated by 200-500 nm. Shatz demonstrated that dipolar and higher multipolar coupling between particles lead to blue shifts when the particles are separated by sufficiently large distances, while when they are closer than 100 nm the static dipolar couplings produce red-shifted plasmon.

External Control of Biomolecular Activity via Covalent Attached Nanocrystal Antennas. (C10.7)

K. Hamad-Schifferli and its group presented their studies concerning the use of metal nanocrystals as antennas for controlling the activity of biological systems. In particular, they presented the biomolecular activity of DNA and proteins controlled by covalent attached 1.4 nm diameter Au nanocrystals.

They heated the nanocrystals by an external magnetic field that induces eddy currents in the nanocrystals. As result, the nanocrystals transfer heat to the biomolecule to which they are attached. They observed that the heating of nanocrystals linked to DNA oligonucleotides in solution produce a localized and reversible.DNA dehybridization.

Nanoscale Particle Arrays Induced by Highly Ordered Protein Assemblies. (C10.10)

S. Behrens and coworkers used biocompatible methods to built-up nanoscale inorganic particle arrays, the inorganic systems have the patterns of the template.

In particular, they reported the formation and binding of noble metal nanoparticles on microtubules that are highly ordered cylindrical protein assemblies. The periodic functional groups of amino acids serve as active sites for nucleation and binding of metallic nanoparticles. The pattern of these nanoparticles reflects the regular arrangements of the tubulin molecules in the microtubule nanoparticle array.

Future Direction of the Symposium

No doubt that nanobiotechnology is just at the beginning of an overwhelming positive future. The combination of natural nano-systems (biomolecules) and artificial nano sized species such as metal or semiconductor nanoparticles opens many doors to novel future applications. In so far it can be assumed that symposia dealing with this or similar topics will become a self-evident part of conferences like MRS.

SYMPOSIUM C

Bio-Inspired Nanoscale Hybrid Systems

December 2 – 4, 2002

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SESSION C1/NN1: JOINT SESSION
ARRAYS, ESSAYS AND DIAGNOSTICS - I
Chair: Guenter Schmid
Monday Morning, December 2, 2002
Room 208 (Hynes)

8:30 AM *C1.1/NN1.1
BIODIRECTED SYNTHESIS OF FUNCTIONAL MATERIALS USING NANOSCALE BUILDING BLOCKS. Chad A. Mirkin, Department of Chemistry and Institute for Nanotechnology, Northwestern University, Evanston, IL.

This presentation will discuss the use of biological structures to guide the assembly of nanoscale inorganic building blocks into functional materials. Assembly strategies that address several length scales, ranging from the nanoscopic, to the microscopic, to the macroscopic will be presented. Some of these novel materials already have shown substantial promise in the area of medical diagnostics. This presentation will discuss their syntheses, structures, and optical and electrical transport properties.

9:00 AM *C1.2/NN1.2
BIOMATERIAL-NANOPARTICLE HYBRID SYSTEMS FOR BIOELECTRONICS. Itamar Willner, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, ISRAEL.

The integration of functionalized nanoparticles or nanotubes with biomaterials yields hybrid systems for bioelectronic and electrical circuitry applications. The reconstitution of apo-redox-enzymes on cofactor-functionalized Au-nanoparticles or carbon nanotubes (CNT) associated with electrode supports yields electrically-contacted protein assemblies. The effectiveness of the electronic coupling between the redox center of the proteins and the electrode will be discussed in terms of the structural features of the different nanoassemblies. DNA provides an attractive template for the construction of nanoscale electronic circuitry. The functionalization of CdS nanoparticles with nucleic acids provides a function label for the optical and photoelectrochemical detection of DNA. The immobilization of double-stranded DNA-CdS nanoparticle assemblies on surfaces provides an important element for the future assembly of semiconductor nanoparticle structures. The incorporation of intercalator-functionalized Au-nanoparticles into double-stranded DNA, or the electrostatic self-assembly of polylysine functionalized with Au-nanoparticles with double stranded DNA yield nanowires of Au-particles in the DNA templates. The possibilities of constructing complex structures consisting of DNA/CNT/nanoparticles will be presented.

9:30 AM C1.3/NN1.3
NANOPATTERNED SURFACES FOR CONTROLLED SELF-ASSEMBLY OF MOLECULES. Federico Rosei, Y. Naitoh, M. Schunack, E. Legsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, C. Joachim, CEMES-CNRS, Toulouse, FRANCE.

Ordering molecular building blocks into a suitable architecture at nano scale is very appealing for the development of future integrated nanoelectronics [1]. We used a large organic molecule called Lander [2] (C90H98), and investigated its electronic states at room temperature (RT) by Scanning Tunneling Spectroscopy (STS) and its Self-Assembly on Cu(110) by Scanning Tunneling Microscopy (STM). The Lander [2] has a central polyaromatic molecular wire, and four "spacer legs" (3,5-di-tert-buthylphenyl) for isolation from the substrate. The four legs are imaged as four lobes with three different conformations by STM, two rhomboidal (chiral) shapes that are mirror symmetric to each other and one rectangular shape. In order to create a suitable template for controlled molecular adsorption, the clean Cu(110) surface was exposed to oxygen to form the oxygen induced (2x1) reconstruction. By dosing a proper amount of Oxygen at 350 C we can make Cu row domains along [001] direction with 2 nm width between 2x1 domains. When the Lander molecules are deposited on this template, the Lander preferentially attaches to bare Cu regions. By tuning molecular coverage in a controlled manner we obtained 1 D molecular nanostructures. This type of directed self-assembly opens new possibilities for ordering organic molecules on surfaces. In a second set of experiments, spectra from isolated Lander molecules on Cu(110) terrace reveal two broad peaks observed at 0.5 V and +0.8 V. These can be associated with the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states of the molecule at RT. References. [1] C. Joachim, J.K. Gimzewski and A. Aviram, Nature 408, 541 (2000). [2] F. Rosei et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002).

9:45 AM C1.4/NN1.4
CONDUCTANCE MICROSCOPY FOR ELECTRIC CONDUCTION STUDY OF BIOINSPIRED HYBRID NANOSTRUCTURES UNDER AMBIENT CONDITIONS. Saleem Rao, Wahyu Setyawan, Seunghun Hong, Florida State Univ, Dept of Physics, Tallahassee, FL.

Recently, the electric conduction mechanism in hybrid nanostructures draws an attention due to the possible applications in bio- and molecular electronics. Several prototype devices based on electric conduction in hybrid systems have been reported. These include biosensors that can selectively detect a few biological molecules and electronic circuit components comprised of organic molecules. However, it is still very difficult to build hybrid electronic devices, and even the conduction mechanism in some molecular units is still controversial. It is partly due to the lack of general tool kits for the assembly and analysis of hybrid nanostructures. We utilized recently developed dip-pen nanolithography to assemble hybrid nanostructures comprised of electrodes and various molecular units such as organic molecules and carbon nanotubes. The electrical properties of assembled hybrid systems are studied via conductance microscopy (CM) that allows us to obtain conductance maps under ambient conditions utilizing a conducting AFM tip. In this presentation, we will show that conductance microscopy can be utilized as a general tool to study 1) intra-molecular electric conduction and 2) the contact resistance between molecular units. Furthermore, we will address several important issues for utilizing CM under ambient conditions including ionic currents and humidity. This effort is aiming for the development of a workhorse technique for bio- and molecular electronics comparable to I-V stations for microelectronics.

10:30 AM *C1.5/NN1.5
DNA-MEDIATED ASSEMBLY OF CARBON NANOTUBE DEVICES. Keith A. Williams, Peter Veenhuizen, Cees Dekker, Delft University of Technology, Department of Nanoscience and DIMES, Delft, THE NETHERLANDS.

We are developing techniques for using DNA as a means for assembling nanodevices from inorganic components, such as carbon nanotubes. To the assembly schemes we envision, DNA contributes molecular recognition, convenient (de)hybridization conditions, and compatibility with existing biotechnological tools, such as gel electrophoresis, enzymatic cutting, and PCR. Recently, we demonstrated attachment of peptide nucleic acid (PNA, a DNA mimick) to single-walled carbon nanotubes. The resulting macromolecules combine the extraordinary electronic properties of nanotubes with the sequence-specific recognition of DNA. This approach provides a means for controlling the connectivity of the nanotubes to nanoelectrodes and to each other, and also offers the prospect of parallel, autonomous assembly of well-ordered nanoscale structures. In this presentation I will discuss current work and prospects for parallel assembly and replication of nanodevice structures.

11:00 AM C1.6/NN1.6
ELECTRONIC DETECTION OF INDICATOR-FREE DNA HYBRIDS BY ELECTRONIC FIELD CONTROL. H.Y. Lee, Y.S. Choi, H. Tanaka, and T. Kawai, The Institute of Scientific and Industrial Research, Osaka University, Osaka, JAPAN.

The electronic detection of a sequence-specific gene using an ultra-sensitive multipotentiostate is of great significance in the biomedical field. DNA microarray enables simultaneous analysis of thousands of sequences of DNA for genetic and genomic diagnostics and gene expression monitoring. As the electrochemical assay method, costs have to be reduced and a reliable detection system has to be integrated in a portable format. Recently, some electrochemical DNA sensors have been developed using electrochemically active DNA intercalates. We will present the research to the development of DNA chip with indicator-free DNA hybrids by using electrochemical response. Cyclic-voltammetry in 100mM phosphates solution at 50mV/s confirmed the immobilization of probe biotinylated DNA on the avidin-treated Au electrodes using direct electric field. When several DNA were detected electrochemically, there was a difference between indicator-free target DNA and control DNA in the redox peak current. It is suggested that our DNA chip can be detected specifically by using the indicator-free DNA hybrids. Advantages of our method are process simplicity. Recently we are extending this work to multi-channel electrochemical DNA chip microarray to reduce its size to palm-top size. And we will present AFM image of oligonucleotides probes in solution.

11:15 AM C1.7/NN1.7
A HIGH PERFORMANCE CELL PATTERNING FOR CELL-BASED SENSOR APPLICATIONS. Mandana Veiseh, Miqin Zhang, University of Washington, Dept of Materials Science & Engineering, Seattle, WA.

Cell-based biosensors have stimulated great interest in the last decade due to their many applications, including bio-warfare toxin detection; drug evaluation; identifying pollutants; viruses, bacteria, and cell

types recognition in health/food industries. Major challenge for the development of such sensors is, to pattern highly selective proteins that retain their bioacitivity and guide natural cell growth. We will use lithography and surface engineering to develop patterned chip-based microdevices, where the patterns preferentially immobilize (or repel) proteins or peptides in desired regions, thus guiding growth of single or a cluster of cells on the surfaces. We will also develop surface modification approaches to design biomimetic surfaces that will sustain natural and long-term cell growth. Micropatterns of gold in shapes of square or strips are precisely fabricated on 2D silicon surfaces by photolithography. Mixed -COOH-terminated self-assembled monolayers (SAMs) are bound to gold regions to conduct covalent immobilization of fibronectin. The silicon regions are modified with polyethylene glycol (PEG) molecules through silanization to prevent cell attachment. Fourier transform infrared spectroscopy (FTIR), fluorescence microscopy and atomic force microscopy (AFM) will be used for characterization of protein patterning step. Selective adhesion of mouse fibroblast, human HeLa and mouse macrophage cells will be examined on patterned substrates. Cell patterned substrates will be visualized by bright filed optical reflectance microscopy. The technique will be able to pattern highly selective and non-denatured proteins to guide natural and uniform growth of a single cell and a cluster of cells - a key factor of high performance sensors. This technique is simple, inexpensive, and compatible to large-scale microdevice fabrications.

11:30 AM C1.8/NN1.8
MOLECULAR CASTING WITH DNA-MEMBRANE COMPLEXES. Hongjun Liang[a], Thomas E. Angelini[b], James Ho[c], Paul Braun[a] and Gerard C.L. Wong[a,b,c], University of Illinois at Urbana-Champaign, Urbana, IL; [a]Department of Materials Science and Engineering; [b]Department of Physics; [c]Department of Bioengineering.

Cationic lipid-DNA complexes can self-assemble into a nanoporous lamellar structure, in which 1-D ordered DNA arrays are intercalated between planar lipid membrane sheets. The DNA spacings can be tuned from 2.5nm to 6.0nm, and essentially define an array of channels with tunable sizes. We have used these DNA membrane complexes as templates for the synthesis of nanostructured CdS, by reacting H_2S with divalent Cd^{2+} ions confined in the inter-DNA channels described above. By tuning the membrane charge density, we found that the condensed Cd^{2+} ion density and the inter-ion spacing can be controlled. The structural evolution of both the CdS and the biomolecular template during the reaction the have been monitored using high resolution synchrotron Small Angle X-ray Scattering (SAXS) and with Transmission Electron Microscopy (TEM). We found that spatially periodic anisotropic CdS structures with domain sizes as large as 0.5μm can be grown. Furthermore, molecular details of the DNA molecule can be observed in the morphology of the templated CdS: The orientation of the polar planes of CdS are aligned with that of the highly charged sugar phosphate backbone of DNA. The use of these hybrid biomolecular systems in the template-directed synthesis of other materials will be discussed.

SESSION C2/NN2: JOINT SESSION
ARRAYS, ESSAYS AND DIAGNOSTICS - II
Chair: Ulrich Simon
Monday Afternoon, December 2, 2002
Room 208 (Hynes)

1:30 PM *C2.1/NN2.1
FABRICATIONS OF PEPTIDE NANOTUBES FUNCTIONALIZED WITH BIOLOGICAL AND MOLECULAR RECOGNITIONS AND THEIR ASSEMBLIES INTO DEVICE CONFIGURATIONS. Hiroshi Matsui, Yung-fou Chen, Ramin Djilali, City Univ. of New York, Hunter College, Dept. of Chemistry, New York, NY.

Non-lithographic fabrications of devices such as electronics and sensor have been studied extensively by assembling nanometer-sized building blocks into the device configurations. While various nanocomponents have been applied as building blocks to construct nanodevices, the more reproducible methods to assemble them onto precise positions are desirable. We have been fabricating peptide-based nanotubes and functionalizing them with various recognition components, and our strategy is to use those functionalized peptide nanotubes, which can recognize and selectively bind a well-defined region on patterned substrates, as building blocks to assemble three-dimensional nanoscale architectures at uniquely defined positions and then decorate the nanotubes with various materials such as metals and quantum dots for electronics and sensor applications. In this presentation, we would like to present the nanotube assemblies using two types of recognitions: a biological recognition and a host-guest molecular recognition. We have demonstrated that the nanotubes can be selectively immobilized on surfaces using protein-protein interactions. Ferrocene-functionalized nanotubes (host) were also observed to recognize an exact ring size of cycledextrin SAMs (guest) on Au surfaces and the attachment/detachment of nanotubes was controlled electrochemically due to the control of redox states of the ferrocene nanotubes, which may be applied as switches.

2:00 PM *C2.2/NN2.2
NANOPARTICLE BIOCONJUGATE CHEMISTRY: STRENGTHENING BIOMOLECULES' GRIP ON GOLD. Sarah Evans, Aimee Erickson, Castro Laicer, Kyle Page, T. Andrew Taton, Department of Chemistry, University of Minnesota, Minneapolis, MN.

Biomolecule-nanoparticle conjugates have been shown to be versatile components of tailorable assembled materials and of biomolecule detection schemes. In many cases, biomolecules are bound to metal and semiconductor surfaces through thiol functionalities; however, the resulting nanoparticle-thiol bonds are kinetically labile and equilibrate with free, unbound biomolecules at temperatures (> 60°C) frequently encountered in materials processing and biotechnological protocols. We report that an intermediary polymer layer can serve not only as a protective shell for aqueous nanoparticles but also as a means for attaching biomolecules more permanently to nanoparticle surfaces. We anticipate that the thermal and chemical stability of these bioconjugates will increase their use in processed composites and harsh biological protocols.

2:30 PM C2.3/NN2.3
SELECTIVITY OF POLYPEPTIDES FOR BINDING TO CARBON NANOTUBES. Siqun Wang, Hong Wang, Steve Lustig, Nancy Rizzo, Shekhar Subramoney, Anand Jagota, DuPont, Central Research, Wilmington, DE; Yet-Ming Chiang, Ellen S. Humphreys, Sung-Yoon Chung, Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA.

We have studied the binding of short polypeptides to a variety of carbon nanotubes and folded graphene structures. A primary technique we have utilized is phage display against multi-walled and single-walled carbon nanotubes. Consensus sequences emerge that depend on the type of nanotube, and differ from control experiments done on single crystal graphite. We find the emergence of sequences with increased content of residues with aromatic groups, e.g., H & W. We will also describe sequence motifs that emerge. Site-directed mutagenesis and experiments with synthesized peptides have been conducted to determine if binding is specific and based on displayed peptides. We also present theoretical calculations of the statistical mechanics of binding between these peptides and nanotube surfaces.

2:45 PM C2.4/NN2.4
A NEW PROTEIN PATTERNING TECHNIQUE AND ITS APPLICATION IN BIO-INSPIRED SELF-ASSEMBLY. Dong Guo, Helen McNally, Purdue University, School of Electrical and Computer Engineering, West Lafayette, IN; Maneesh Pingle, Donald Bergstrom, Purdue University, Dept. of Medicinal Chemistry and Molecular Pharmacology, West Lafayette, IN; Rashid Bashir, Purdue University, School of Electrical and Computer Engineering, West Lafayette, IN.

Protein patterning techniques are crucial for the development of antibody-based biosensor and the study of controlled cell growth. This paper discusses a new protein patterning technique based on microelectronic fabrication, DNA hybridization and biotin-streptavidin pair. A gold-on-silicon-dioxide substrate with micron size pattern was fabricated with photolithography and lift-off process. The average surface roughness of the gold pattern is 4.3 nm, measured by contact mode AFM. Thiol derivatized single stranded DNA was attached to the gold pattern surface by the chemical bonding between gold atom and sulfur atom. Surface attached DNA was then hybridized with a biotin conjugated complementary DNA sequence. Thus, the gold pattern was translated into a biotin pattern with similar resolution. Fluorescein conjugated streptavidin was patterned as demonstration. Fluorescence microscopy shows relative uniform streptavidin coverage of micron resolution and low background non-specific binding. The proposed protein patterning technique takes advantage of the high resolution of modern microelectronic fabrication. It has the potential of reaching submicron resolution. The biotin-streptavidin pair provides extremely specific and stable linking for protein immobilization. To show its application in biological inspired self-assembly, this technique was used successfully in the self-assembly of 20 nm streptavidin conjugated gold particles.

3:00 PM C2.5/NN2.5
SPECIFIC INTERACTION BETWEEN A PROTEIN AND CARBON NANOTUBES - TOWARDS BIOSENSORS. Carolina Salvador-Morales, Trinity College, Dept of Physics, Dublin, IRELAND; Ed Franklin, Trinity College, Dept of Biochemistry, Dublin, IRELAND; G. Chambers, DIT, School of Physics, Dublin, IRELAND; Antonio Fonseca, Janos Nagy, FUNDP, Namur,

BELGIUM; Werner Blau, Andrew Minett, Marc in het Panhuis, Trinity College, Dept of Physics, Dublin, IRELAND.

Functionalised carbon nanotubes are being investigated for use as transducers in sensing applications, which has the potential increase sensitivity and real-time detection of biological entities. Several proteins and their interaction with single walled and multi walled carbon nanotubes (SWNT / MWNT) were investigated. It was found that specific interaction between carbon nanotubes and proteins such as Biliverdin IXb reductase (BVRB), could be induced using non-covalent functionalisation of SWNT and MWNT. A novel method for separation according to weight of these biologocial hybrid systems is described. Gel electrophoresive and Raman spectroscopy showed that these hybrid systems contain both nanotubes and BVRB. Using Raman spectrocopy it was found that the hydrophilic surface of BVRB interacts (specifically) with the hydrophilic surface of functionalised carbon nanotubes. Activity investigations showed that BVRB remains bio-active in the hybrid system. Selective interaction of a protein with nanotube was achieved through functionalisation. The molecular interaction was investigated using Raman spectroscopy. This is an important first step towards using carbon nanotubes in sensor applications.

SESSION C3: ARRAYS, ESSAYS AND DIAGNOSTICS - III
Chair: Ulrich Simon
Monday Afternoon, December 2, 2002
Room 208 (Hynes)

3:30 PM C3.1
HIGH DENSITY MAGNETIC RECORDING ON PROTEIN-DERIVED NANOPARTICLES. J. Hoinville, A. Bewick, D. Gleeson, R. Jones, O. Kasyutich, A. Nartowski, B. Warne, J. Wiggins, and K.K.W. Wong, and E. Mayes, NanoMagnetics Ltd., Bristol, UNITED KINGDOM.

This paper reports on the progress in developing self organized nanoparticulate arrays for magnetic recording at densities beyond 30 Gbit/cm^2 (200 Gbit/in^2), and in particular describes the beneficial use of biological templates in developing such arrays. Chemically synthesized, high magnetocrystalline anisotropy magnetic nanoparticles have demonstrated extremely narrow size distributions that are critical in reducing media noise. Due to their monodispersity, they also exhibit emergent self-patterning that could potentially support bit-per-particle densities up to 2-8 Tbit/cm^2 (10-50 Tbit/in^2). High anisotropy $L1_0$ CoPt precursor grains are prepared within apoferritin from aqueous reactants, with synthesis conditions controlling grain size, structure and composition. Smooth films on glass disk substrates are produced by either spin- or dip-coating from aqueous dispersions of the precursor material. Films are typically annealed at 590°C for 60 minutes with a 19 kPa (190 mBar) partial pressure of H_2 to form the $L1_0$ phase. We report on recently produced films that have demonstrated moderate-density recording using a contact drag tester with commercial, 0.35 μm-wide magnetoresistive (MR) heads. The highest areal density currently achieved for these nanoparticulate films is 0.93 Gbit/cm^2 (6.0 Gbit/in^2).

3:45 PM C3.2
PEPTIDE-MEDIATED SYNTHESIS OF MAGNETIC MATERIALS. Brian D. Reiss, Chaunbin Mao, Anuj Aggarwal, Daniel J. Solis, Angela M. Belcher, Center fo Nano-, and Molecular Science, University of Texas at Austin, Austin, TX.

Ultrafine magnetic nanoparticles have numerous applications in magnetic memory devices, biosensors, and nanoscale elctronics. Currently such materials are prepared as colloidal sols, and while these preparations yield monodisperse, crystalline solids, the dispersions are often expensive to prepare and usually lack long-term stability, limiting their applications. For this reason alternative synthetic strategies are currently under investigation. Peptide mediated synthesis of magnetic nanoparticles is one such alternative since it has previously been used to successfully synthesize semiconducting nanoparticles and since it should provide a low temperature alternative to the traditional preps of magnetic nanoparticles. To accomplish this goal, two combinatorial phage libraries were exposed to the surfaces of nanoparticulate thin films of magnetic materials. These phage libraries contained phage which were functionalized with either a random12 mer or 7 mer peptide attached to their P3 coat proteins. To date, the L10 phase of FePt and CoPt have been investigated, as well as the ϵ phase of Co. Peptides have been isolated and identified which selectively bind to each of these surfaces. These peptides were then used to control the nucleation of nanoparticles of these materials, and nanoparticles of the $L1_0$ phase of CoPt and FePt have been prepared using these peptides as templates to control the crystallinity of the nanoparticles. These particles have been extensively characterized using high resolution TEM and SQUID magnetometry.

4:00 PM C3.3
SUPERPARAMAGNETIC NANOPARTICLES FOR IMAGING. Nathan Kohler, Yong Zhang, Miqin Zhang, University of Washington, Dept of Materials Science, Seattle, WA.

Our previous work has shown that grafting folic acid on superparamagnetic magnetite nanoparticles increases their uptake into cancer cells in vitro. In this work, we will develop superparamagnetic nanoparticle conjugates that would serve a dual purpose both as contrast enhancement agents in magnetic resonance imaging (MRI) and as drug carriers in controlled drug delivery for cancer diagnostics and therapeutics. Superparamagnetic particles are first surface-modified with polyethyleneglycol (PEG) via a self-assembly technique. The PEG on the nanoparticles will not only improve the particle's blood biocompatiblity and increase their circulation time in blood, but also prevent nanoparticle agglomeration. When further immobilized with therapeutic drugs (e.g., methotrexate), they would function as drug carriers that can be monitored continuously with MRI while the treatment is in progress. Methotrexate, a folate analog, is known to achieve the particle uptake utilizing the same cell receptor as folic acid. Controlled drug release will be tested in phosphate buffered solution, simulated body fluid (SBF), and enzyme solution. The efficacy of drug delivery by nanoparticle-PEG-MTX to tumor cells will be also examined. Characterization of functionalized nanoparticles will be conducted using FTIR and Electron Energy Loss Spectroscopy (EELS). Further, drug delivery will be studied as a function of pH using UV-VIS spectroscopy. Nanoparticle uptake into BT20 cells will be visualized by optical and transmission electron microscopy (TEM) and quantified by inductively coupled plasmon resonance spectroscopy (ICP). Cell viability will be further analyzed to quantify the effectiveness of the drug delivery system in vitro.

4:15 PM C3.4
BIOTEMPLATE-DIRECTED 2-DIMENSIONAL NANOSTRUCTURE ASSEMBLY. Seungju M. Yu, Xiao Mo, Johns Hopkins University, Dept of Materials Science and Engineering, Baltimore, MD; Mark P. Krebs, Illinois State University, Dept of Biological Sciences, Normal, IL.

There are manifest scientific and technological interests in organizing nanocrystals(NC) into controlled architectures and work is rapidly expanding in exploiting opportunities through self-assembly processes. In this research, we have applied biologically assembled nano-scale template to direct formation of precisely defined 2D nanocrystal arrays. We explored purple membrane (PM), a naturally occurring membrane protein (bacteriorhodopsin, BR) crystal patch from halobacteria, as a precisely structured nanometer-scale template. We have developed genetically engineered PMs that display unique functional groups (e.g. cystein or histidine) on the membrane surfaces with precisely defined nano-scale symmetry. These reactive functional groups were used as specific anchoring sites for NC immobilization. We show that the cystein and histidine mutants of BR mutated at the surface of the PM are capable of forming stable PM-like hexagonal crystal lattices in the bacterial cell membrane. These crystal patches were easily purified by ultracentrifuation and were used to react with functionallized gold nanoclusters. We also present the variation of mutant crystal lattice by detergent treatment and recrystallization techniques. The PM has been known to posses good materials properties and it will allow formation of robust nanocrystal array that can withstand variety of optical and electrical characterization conditions.

4:30 PM C3.5
FABRICATION AND APPLICATION OF PROTEIN CRYSTAL MICROARRAYS 1: DEMONSTRATION OF LASER MANIPULATION AND PATTERING OF PROTEIN CRYSTAL. Yoichiroh Hosokawa, Satoshi Matsumura, Chie Matsubara, Hiroshi Masuhara, Osaka Univ, Dept of Applied Physics, Frontier Research Center, and Venture Business Laboratory, Osaka, JAPAN; Keiko Ikeda, Protein Crystal Corp, Osaka, JAPAN; Ai Shimo-oka, Kyoto Inst of Tech, Dept of Applied Biology, Kyoto, JAPAN; Hajime Mori, Protein Crystal Corp, Kyoto Inst of Tech, Dept of Applied Biology, Kyoto, JAPAN.

The proteomics technique has received significant attention as an important technique for disease diagnosis and for monitoring drug efficacy and safety. To realize the high-throughput analysis of proteins expression, preparation of protein microarrays is strongly requested, however, it is very difficult in comparison with DNA microarrays because of complex structures of proteins. Recently, we have been interested in applying protein crystal of polyhedra, which are μm-size proteinaceous occlusion bodies produced by insect viruses, for immobilization of functional proteins. On the other hand, a laser trapping technique based on the photon pressure has received much

attention as a technique to manipulate biocells and microparticles. Recently, furthermore, we have already succeeded photothermal fixation of polymer microparticles onto a polymer substrate by local heating due to UV laser irradiation. It is considered that the polyhedra crystals are very useful to fabricate protein microarrays and we demonstrated here that the polyhedra crystals of a few μm could be fixed one by one on a slide glass by laser manipulation technique. Aqueous solution containing the dispersed polyhedra crystals was set on the microscope stage and each crystal was trapped by a focused 1064 nm beam of a Nd^{3+}: YAG laser. On the trapped polyhedra, femtosecond laser was irradiated to fix it on a polymer substrate. Damages of the polyhedra crystals will be decreased by adjusting femtosecond laser and noncontact pattering of the polyhedra crystal is realized with the precision less than 1 μm.

4:45 PM C3.6
FABRICATION AND IMAGING OF PROTEIN CROSSOVER STRUCTURES. J.R. LaGraff[a], Y.-P. Zhao[b], D.J. Graber[c], D. Rainville[d], G.-C. Wang[b], T.-M. Lu[b], D. Szarowski[c], W. Shain[c], J.N. Turner[c]; [a]Department of Chemistry, Hamilton College, Clinton, NY; [b]Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY; [c]Wadsworth Center, Albany, NY; [d]Department of Physics, Siena College, Loudonville, NY.

Proteins often deform, transfer charge, dehydrate or otherwise denature when adsorbed or patterned directly onto an inorganic substrate, thus losing specificity and biofunctionality. One method used to overcome loss-of-function is to pattern the protein of interest directly onto another underlying protein that acts as a buffer layer between the substrate and the desired protein. We have used microcontact printing (μcp) to cross-stamp orthogonal linear arrays of two different proteins (e.g., IgG, EGF, poly-lysine, protein A, streptavidin) onto glass substrates. This creates three separate types of protein-substrate microenvironments, including crossover structures of protein one on protein two. These structures were characterized for structural integrity using primarily *in situ* scanning force microscopy (SFM), while fluorescence labeling and optical microscopy were used to assess biological activity at the molecular and cellular levels. Particular attention was given to the systematic variation of μcp pattern design, stamping conditions, and the chemical, physical, and biochemical modifications of the glass substrate prior to μcp, and their subsequent influence on structural features and function of μcp proteins at the molecular-level. (Partially supported by NSF's NanoBioTechnology Center, Cornell University NSF-9876771 and NSF-DMR9971265. This work was performed in part at the Cornell Nanofabrication Facility NSF-ECS-9731293.)

SESSION C4: ARRAYS, ESSAYS AND DIAGNOSTICS - IV
Chair: Stephan J. Stranick
Tuesday Morning, December 3, 2002
Room 208 (Hynes)

8:30 AM *C4.1
BIO-ASSEMBLY OF NANOSCALE MATERIALS FOR NANOELECTRONICS. Ming Zheng, DuPont Central Research & Development, Wilmington, DE. ♣

One of the fundamental issues in nanoelectronics is how to register component materials by design in the nano-meter scale. Bio-macromolecules such as protein and DNA are information rich, capable of self-assembly, subject to atomic level engineering and compatible in size with inorganic nano-materials. These attributes make them ideal molecular tools for programmable assembly of nano-materials. In this presentation, I will give an overview of our multi-disciplinary effort at DuPont on biomolecular assembly of nanoparticles and nanotubes. I will describe advances we have made in engineering specific interactions between biomolecules and inorganic nano-materials, in using biomolecules to control the composition and geometry of nano-material assemblies, and in applying biochemical techniques for processing and analysis of nanoparticles and nanoparticle-biomolecule complexes. Examples of interesting nanoparticle assemblies constructed will be given. Design of device architectures that are consistent with our bio-assembly scheme will also be discussed.

9:00 AM C4.2
PATTERNED POLYMER COMPOSITE MICROSRUCTURES FOR BIOLOGICAL APPLICATIONS. Haipeng Zheng, Michael C. Berg, Michael F.*Rubner, and Paula T. Hammond, Department of Chemical Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Recently we developed new techniques including polymer-on-polymer stamping to create patterned functional polymer surfaces on a number of substrates. We can utilize these surfaces as a basis for the selective deposition of colloidal particles through electrostatic and secondary interactions. To apply this process in the areas of tissue engineering, cellular biosensor and high throughput drug screening assays, we have designed a specific polymer-colloid system for patterning RGD peptides and mammalian cells. The surface of poly(acrylic acid) /poly(allylamine hydrochloride) multilayer films constructed specifically to prevent cell adhesion is patterned, and used to direct colloidal particles that can act as a functional template to control cell adhesion and spreading. The effect of pattern geometry and topography of colloidal arrays on cell attachment and behavior will be discussed by tuning the particle size, the particle packing density and the dimension of the colloidal patterns.

9:15 AM C4.3
ARRAYING OF INDIVIDUAL CELLS USING DIELECTRO-PHORESIS. Darren S. Gray and Christopher S. Chen, Dept of Biomedical Engineering, Johns Hopkins University, Baltimore, MD.

Positioning of individual cells has multiple applications including the study of the cell-biomaterial interface. An arraying technique which allows reliable control over cell numbers and the alignment of cells with detection elements is especially important for the construction of high throughput applications. We have developed a method to move living mammalian cells safely and rapidly to precise locations by applying potentials of 1-5 V at 2MHz to an electrode array constructed with standard microfabrication techniques. Within a few minutes, cells are trapped at field maxima by dielectrophoresis (DEP), the force on polarizable bodies in a nonuniform electric field. Using DEP, we are able to form arbitrary arrays of single cells on planar surfaces. The electric fields involved are analyzed with finite element methods, confirming that field maxima exist at trap locations. DEP will be demonstrated both alone and in conjunction with micropatterned surface chemistry as a powerful tool for cell manipulation. Applications ranging from cell-surface and cell-cell interactions to high throughput screening will be discussed.

9:30 AM C4.4
NANOSTRUCTURED ARRAYS OF ARTIFICIAL SYNAPSES FOR CONTROL OF T CELL ACTIVATION. Junsang Doh and Darrell J. Irvine, Massachusetts Institute of Technology, Dept of Materials Science & Engineering/Biological Engineering Division, Cambridge, MA.

T cell activation normally occurs via the formation of an immunological synapse, an organized array of signaling proteins accumulated at the interface between a T cell and an antigen-presenting cell (APC). One way to treat diseases such as cancer, hepatitis C, or HIV that interfere with T cell activation is via adoptive transfer: activation and expansion of a pool of donor T cells ex vivo that is subsequently infused into a patient to boost immunity. However, typical approaches of ex vivo T cell activation using antibodies provide a non-natural stimulus that limits the expansion of donor cells, activates the cells in an antigen-nonspecific manner, and results in a short-lived phenotype for the transferred cells- providing only temporary benefit to the recipient and an increased risk of autoimmunity. We are studying a biomimetic approach, using synthetic surfaces to mimic the organization of signaling proteins on the APC surface in order to obtain robust expansion of antigen-specific T cells that have a long-lived phenotype. Patterned surfaces have been fabricated that present regular arrays of "artificial synapses", each composed of a 2D array of monodisperse poly(methyl methacrylate) nanospheres, functionalized with different APC-derived signaling proteins. Surfaces were prepared by a multi-step process: nanospheres with surface charged groups and ligands for protein immobilization were synthesized, electrostatically adsorbed as a monolayer onto a polyelectrolyte-coated substrate, microcontact printed to pattern the monolayer into discrete "synapses", and functionalized with signaling proteins. Characterization of assembled surfaces by scanning electron and fluorescence microscopies has shown that complex signaling protein patterns can be created. Examination of T cell interactions with these devices by time-lapse fluorescence microscopy has revealed that activation of T cells can be finely controlled by the composition and structure of these biological/synthetic polymer hybrid substrates.

9:45 AM C4.5
PROTEIN/POLYMER HYBRIDS AS BIOMIMETIC VALVES. Jacob Schmidt, Dean Ho, Carlo Montemagno, UCLA, Dept of Bioengineering, Los Angeles, CA.

Membrane channel and pore proteins are nanometer-sized pumps and valves, transporting ions and molecules selectively based on size, charge, or type. Some of these proteins actuate in response to an applied voltage, a property which immediately suggests possible device applications. The short functional lifetimes of proteins in lipids necessitates the use of biocompatible polymers which mimic the

natural environment of the protein sufficiently that function is retained. We have genetically engineered a voltage-gatable pore protein and inserted it into monolayer planar membranes of amphiphilic block copolymers. Particularly crucial is the orientation of the proteins within the membrane; fully gatable transport is not possible with unoriented protein. We present our recent work in engineering this hybrid protein/polymer system. We have characterized the porin and protein/polymer complex at the nanometer and micrometer length scales. We show the results of electrical and analyte transport experiments demonstrating the gating ability and the degree of protein orientation within the membrane. We discuss the implications of these experiments and prospects for devices functionalized with nanoscale valves or polymers having controllable porosity.

SESSION C5: MINERALISATION, IMPLANTS AND SURFACES - I
Chair: Stephan J. Stranick
Tuesday Morning, December 3, 2002
Room 208 (Hynes)

10:30 AM *C5.1
SIMULATION AND PREDICTION OF NEW MATERIAL PROPERTIES AND BIOLOGICAL REACTIVITY BY MOLECULAR MODELLING OF THE INTERACTION OF BIOPOLYMERS WITH SOLID SURFACES. Hubert Kuhn, Maria Leis, University of Essen, Dept Physical Chemistry, Essen, GERMANY.

The understanding of the interaction of proteins with metal and polymer surfaces is of essential meaning to the prediction of the compatibility of new materials with the biological environment. The dynamics of the protein adsorption and the interaction with these materials decide the histocompatibility of biomaterials in medical applications. The molecular processes of the interactions between proteins and solid-surfaces are not well understood. However, these phenomenons are the basis for development and improvement of new implants and other materials for application in biological systems. Theme of this talk is the investigation of the specific interactions of proteins with molecular modelling and molecular dynamics techniques on an atomistic and molecular scale. The main focus is on the calculations of molecular structures and the adsorption of proteins at metal and polymer surfaces in aqueous solution. The intention of this presentation is a contribution to a better understanding of the behaviour of different material classes in biological systems. Additionally, the methods and results for calculation of energies, conformations and structures of other classes of adsorbed Biopolymers at solid surfaces which are suitable for the development of new materials in medical applications will be presented.

11:00 AM C5.2
NANO-FIBROUS SCAFFOLDING ARCHITECTURE ENHANCES PROTEIN ADSORPTION AND CELL ATTACHMENT. Kyung Mi Woo, Victor J. Chen, Peter X. Ma, Department of Biologic and Materials Sciences, University of Michigan, Ann Arbor, MI.

Tissue engineering is a promising approach to resolve the problems faced by transplantation such as the shortage of donor tissues (organs) and immune rejection. Scaffolds (artificial extracellular matrices) play critical roles in tissue engineering. The scaffold is a substrate for cells to attach on, serves as a template for tissue regeneration in 3D, and should finally be replaced by the cell-produced extracellular matrix. Recently, we developed nano-scaled fibrous poly(L-lactic acid) (PLLA) scaffolds under the hypothesis that synthetic nano fibrous scaffolding, mimicking the structure of natural collagen fibers, could create more favorable microenvironment for cells. In this work, features of the nano-scaled fibrous polymer scaffolds were studied in relation to protein adsorption, which mediates cell interactions with scaffolds. Nano-scaled fibrous scaffolds adsorbed 4-fold higher amount of serum proteins than solid-walled scaffolds did. In addition, these nano-scaled fibrous scaffolds made from the same PLLA material showed a different profile of serum protein adsorption from solid-walled PLLA scaffolds, as revealed by SDS-PAGE. Nano-fibrous scaffolds appeared to have more specific features for protein-binding than solid-walled scaffolds. Western blot analyses confirmed that the nano-fibrous scaffolds adsorbed higher amounts of fibronectin and vitronectin from serum, which are important mediators of cell attachment to structural extracellular matrix components, than the solid-walled scaffolds did. Furthermore, 1.7-fold more MC3T3-E1 cells (an osteoblastic cell line) attached on the nano-scaled fibrous scaffolds than on the solid-walled scaffolds (both scaffolds were pre-treatment in fetal bovine serum). These results suggest that the biomimetic nanoscaled fibrous architecture selectively enhances protein adsorptions, and leads to more favorable microenvironment for cell-extracellular matrix and cell-scaffold interactions.

11:15 AM C5.3
CONTROL OF CELL ADHESION ON MICROPATTERNED WEAK POLYELECTROLYTE MULTILAYERS. Michael C. Berg, MIT, Dept of Chemical Engineering, Cambridge, MA; Sung Yun Yang, Jonas D. Mendelsohn, MIT, Dept of Materials Science and Engineering, Cambridge, MA; Paula T. Hammond, MIT, Dept of Chemical Engineering, Cambridge, MA; Michael F. Rubner, MIT, Dept of Materials Science and Engineering, Cambridge, MA.

Thin films made from weak polyelectrolyte multilayers were patterned with biological ligands using such techniques as microcontact printing and inkjet printing to locally alter the surface interactions with mammalian cells. Specifically, this work focuses on patterning surfaces our group has found to be bio-inert (resistant to fibroblasts) to present specific areas for cell adhesion. The bio-inert surfaces consist of multilayer films made from either polyacrylic acid (PAA) and poly(allylamine hydrochloride) (PAH) or PAA and polyacrylamide (PAAm). We have been successful in microcontact printing and inkjet printing PAH onto these surfaces when PAA is the top layer of the film. The transfer of material is monitored using atomic force microscopy (AFM) and dye surface staining. Ligands containing the adhesion peptide, RGD, can be tethered onto the primary amine groups of PAH to promote fibroblast adhesion. Varying the reaction conditions leads to control over the RGD density, which can be monitored by changes in UV-VIS adsorption and fluorescence microscopy. NR6WT cells (mouse fibroblasts) were seeded on patterned surfaces presenting various RGD densities with an inert multilayer background to study such activities such as motility and spreading. The observed cell interactions are indeed RGD specific since the fibroblasts detached in the presence of soluble RGD. The specificity of the cell interactions was also confirmed by substituting a ligand, which is not known to promote adhesion. The ultimate goal of this work is to develop surfaces that can be employed in biosensor or tissue engineering applications.

11:30 AM C5.4
NANO-SCALE MODIFICATION OF METAL SURFACES FOR BIOMEDICAL APPLICATIONS. Anna Marie Lipski[b], Hoon Choi[b], James Ferris[b], Douglas Yates[b], I-Wei Chen[b] and V. Prasad Shastri[a,b], [a]Joseph Stokes Jr., Research Institute, Children's Hospital of Philadelphia, Philadelphia, PA and [b]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

The use of metals and their alloys in medicine range from implants, to drug delivery devices to pacemakers. Examples of metallic implants include orthopaedic prosthesis and fixative devices for facial reconstructive surgery. Besides playing a structural role, implants by virtue of their proximity to tissue are ideally suited as vehicles for the delivery of bioactive agents, either locally to the diseased tissue or systemically to the patient. In view of the benefits of implant-based delivery of bioactives, presentation of biologically relevant information on an implant surface will become an important factor in future implant development. However, metals are difficult candidates for surface modification due to the lack of functionalizable groups. Therefore, in order to explore and exploit the advances in molecular medicine towards improving the efficacy and performance of metallic medical devices, new surface modification technologies have to be developed. We have developed a novel procedure for nano-scale modification of metal surfaces such that they are rendered amenable to the attachment of biological relevant moieties, such as peptides and growth factors. This modification procedure can be used to generate surfaces rich in amine functionality. Salient features of this modification technique include: 1. Room temperature application 2. Excellent reproducibility with respect to topology and surface chemistry 3. Very high concentration of reactive groups on the surface, and 4. Excellent cell compatibility.

11:45 AM C5.5
PROCESSING MICRO- AND NANO-COMPOSITES OF HYDROXYAPATITE AND POLY(LACTIC ACID). Rodney Priestley, Antonio Senador, Polymer Program, Dept of Chemical Engineering, Institute of Materials Science, Univ of Connecticut, Storrs, CT; Mei Wei, Dept of Metallurgy and Materials Engineering, Institute of Materials Science, Univ of Connecticut, Storrs, CT; Montgomery Shaw, Polymer Program, Dept of Chemical Engineering, Institute of Materials Science, Univ of Connecticut, Storrs, CT.

Hydroxyapatite (HA) is the main component of bones and teeth. As a bioactive material, it has been widely used in many biomedical applications. It has the capability of enhancing bone ingrowth in vivo. Poly(lactic acid) (PLA) has also received considerable attention because of its biocompatible and bioresorbable characteristics. A system comprising HA/PLA features has combined attractive properties of the above two materials, including excellent biocompatibility, controllable biodegradability, and superior osteo-conduction of bone tissue into the implant. Past attempts to reinforce polymers with HA particles have met with varying degrees of

success, with many of the difficulties attributable to poor interaction of the hydrophilic HA particles with an organic polymer matrix. In turn, this leads to agglomeration of HA particles during mixing and low tensile strength of the resulting material. To address these issues, processing technology has focused mainly on modification of the high-energy surface of the ceramic particles with substances that can reduce the surface energy and promote adhesion. In this study, we have investigated alternative processing methods to move the particle size distribution into the nano range while protecting against re-agglomeration using surface active agents. The method to be discussed includes solvent-based dispersion, high-energy impact dispersion, and elongational-flow melt mixing.

SESSION C6: MINERALISATION, IMPLANTS AND SURFACES - II
Chair: Seunghun Hong
Tuesday Afternoon, December 3, 2002
Room 208 (Hynes)

1:30 PM *C6.1
NANOSTRUCTURING OF SURFACES USING ANODIC ALUMINA MEMBRANES — METHODS, MATERIALS AND PROPERTIES.
Thomas Sawitowski, AlCove Surfaces GmbH, Gladbeck, GERMANY.

Since the discovery that cleanability is not necessarily linked to smoothness or gloss of surfaces it is interesting to take a closer look at methods allowing surfaces to be structured on a micrometer and nanometer scale. This discovery is based on the observation that plant leaves for example from the sacrificed lotus or insect wings are structured and thus exhibit an improved cleanability. Other bio-surfaces like the eyes of moths are structured as well. Those surfaces show a reduced light reflection. In all cases those surfaces are interfaces with a desired surface structure allowing the improvement of the surface properties. To achieve those improvements methods to nanostructure surfaces in the sub-500 nm range a needed. Beside very sophisticated lithographic methods the use of nanoporous alumina as a mask to structure surfaces is an easy and feasible way to create those structures on very different surfaces. The unique pore structure of anodic alumina represents an ideal and cheap master to be used to create nanopillars on top of very different materials like polymers, metals or sol-gel-coatings. These masks are used either as imprinting stamps or as masks in injection moulding given rise for a fast and easy method for sub-500 nm structuring.

2:00 PM C6.2
NANOSTRUCTURED AND AUTO-REGENERATING HYBRID INORGANIC/POLYMER COATINGS FOR A DURABLE SELF-CLEAN EFFECT IN OPTICAL QUALITY.
K. Reihs, O. Stahlschmidt, P. Cavaleiro, R. Claessen, SuNyx Surface Nanotechnologies GmbH, Cologne, GERMANY; A. Duparre, Fraunhofer-Institut Angewandte Optik und Feinmechanik IOF, Jena, GERMANY.

Inspired by cicada wings and certain plant leaves, the authors are developing a self-cleaning coating for a broad range of applications. It is for the first time, that these hybrid inorganic/polymer coatings can provide the self-cleaning functionality in optical quality and with a long lifetime, which is an order of magnitude longer than current technology. The coating system consists of inorganic protective coating with a defined nanoscale roughness with an underlying polymeric replenishment layer. This replenishment layer contains a surfactant in a polymer matrix, which diffuses to the top surface of the inorganic thin film through diffusion channels and provides a hydrophobic surface chemistry. Together with the nanoscale roughness, ultrahydrophobicity is achieved with contact angles of 150 - 175°. Due to the continuous self-regeneration of the surface chemistry by self-assembly and diffusion of the surfactant, a much longer lifetime can be obtained as compared to the current technology offering only static coatings, which are prone to degradation. The herein presented coating technology also offers a self-clean function in optical quality for the first time. With regard to transparency as well as light scattering, this coating technology is superior to current products. The total scatter can be lower than 1%. Our research efforts toward this novel concept are presented and feasibility studies are illustrated.

2:15 PM C6.3
SYNTHESIS OF NOVEL ORGANOSILICATE NANOPARTICLES AND THEIR EFFECTS ON OSTEOBLAST BEHAVIOR.
Suniti Moudgil and Jackie Y. Ying, Massachusetts Institute of Technology, Department of Chemical Engineering, Cambridge, MA.

Doped silicate materials such as Bioglass have been recognized in orthopedic medicine for their ability to bond quickly and strongly to bone. However, their clinical applications have been limited due to high-temperature processing conditions and low mechanical strength. We have synthesized materials of similar compositions through low-temperature sol-gel techniques for use as a void-filling cement. While the bulk materials increased cell proliferation, these monoliths remained reactive under aqueous conditions, thus limiting their in vivo potential. In order to exploit the advantages of the sol-gel technique while ensuring more complete reaction of the sol-gel monomer at low temperatures, we have minimized the reaction domains by synthesizing nanoparticles with compositions similar to those of Bioglass. Monodisperse organosilicate particles of 10 nm - 1 micron have been successfully achieved. With the flexible surface chemistry of silicates, these particles can be easily functionalized with various organic groups. These nanoparticles are being investigated for use as a filler for polymer cements to enhance mechanical strength, and as a colloidal suspension to elicit specific osteoblast behavior. The effects of particle size, concentration, and surface chemistry on the mechanical properties of a polymethylmethacrylate (PMMA) matrix have been studied. Low loadings of nanoparticles have been shown to increase both the Vickers hardness and bending strength of PMMA. Particle size and composition have also been shown to affect MC3T3 osteoblast behavior. Cell culture experiments indicated that some organosilicate particles significantly increased osteoblast proliferation. Subsequent investigation with transmission electron microscopy (TEM) showed that certain nanoparticles entered the cell cytoplasm. The mechanism for nanoparticle uptake and its effect on cellular protein expression will be discussed in this presentation.

2:30 PM C6.4
NANOPARTICULATE HYDROXYAPATITE ENHANCES THE BIOACTIVITY OF A RESORBABLE BONE GRAFT SUBSTITUTE.
Stephen A. Doherty, David D. Hile, Donald L. Wise, Debra J. Trantolo, Cambridge Scientific, Inc., Cambridge, MA; Kai-Uwe Lewandrowski, Massachusetts General Hospital, Orthopaedics Research Laboratory, Boston, MA; Jackie Y. Ying, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA; Stephen T. Sonis, Harvard School of Dental Medicine, Dept of Oral Medicine and Diagnostic Sciences, Boston, MA.

Hydroxyapatite is known as a bioactive agent as defined by its osteoconductivity. It was hypothesized that the use of a nanoparticulate form of hydroxyapatite (HA) would enhance not only the bioactivity but also the mechanical properties of bone repair systems. A synthetic system based on the resorbable polymer, poly(propylene fumarate) (PPF) augmented with nanoparticulate HA was designed to meet clinical biomaterial demand for bone reconstruction, while enhancing bioactivity. An in vivo screening study tested bone cell penetration and mechanical stability as a function of HA particle size at bone repair sites. Rat tibial defects were filled with the synthetic PPF-based bone graft substitute augmented with either nanoparticulate HA (median particle size 40 nm) or microparticulate HA (median particles size 26 μm). Histologic analysis performed at three weeks postoperative indicated that incorporation of nanoparticulate HA improved implant biocompatibility and osteointegration. The New Bone Volume Index (relative percentage of new bone at the repair site) was enhanced in defects filled with nanoparticulate HA-augmented graft substitutes (48 ± 15) versus implants containing microparticulate HA (34 ± 11). The study demonstrated the concept that nanoparticulate hydroxyapatite may be used to enhance bioactivity and mechanical properties of the PPF-based bone graft substitute.

2:45 PM C6.5
BIOMIMETIC POLY(L-LACTIC ACID) SCAFFOLDS WITH INTERCONNECTED MACROPORES, COLLAGEN-LIKE NANO-SCALE FIBERS, AND BONE-LIKE APATITE.
Victor J. Chen, Peter X. Ma, University of Michigan, Dept of Biomedical Engineering, Biologic and Materials Sciences, and Macromolecular Science and Engineering Center, Ann Arbor, MI.

Each year, over one million individuals in the United States require surgery on bone fracture or damage-related problems, including fractures with bone loss, fractures that do not heal, and fractures due to bone tumors. Tissue engineering is a new approach that could potentially become a replacement for current therapies such as bone grafts or other artificial devices used to repair bone injuries. In this approach, cells are seeded in a porous scaffold that serves as a template for tissue regeneration. The scaffold degrades after the tissue is formed. Here, we have fabricated porous osteoconductive scaffolds that have well-defined architectures at three different size scales: (i) interconnected spherical pores ~250-400 microns in diameter; (ii) fibrous collagen-like matrix with fibers 50-500 nm in diameter; and (iii) carbonated bone-like apatite particles at the nanometer to micrometer scales. The macroporous interconnected architecture was created with a three-dimensional mold of thermally-bonded paraffin microspheres. A poly(L-lactic acid) (PLLA) solution was cast over the paraffin mold and underwent a rapid thermal phase separation to form nano-scale fibers that mimic the fibrous structures of natural

collagen. To improve the osteoconductivity of these scaffolds, they were incubated in a buffered simulated body fluid at 37°C for several days to allow for in situ apatite formation. It was seen that over time, the apatite particles increased in size. In addition, the growth of apatite particles on the nano-fibrous scaffolds was compared with the growth of particles on similar porous PLLA scaffolds with a solid-walled (not nano-fibrous) morphology. It was seen that the initial number of particles per unit area and the overall increase in mass of the scaffolds were significantly higher in the nano-fibrous scaffolds than in the solid-walled scaffolds. These novel scaffolds may serve as superior support for bone tissue regeneration.

SESSION C7: BIOMATERIALS - I
Chair: Seunghun Hong
Tuesday Afternoon, December 3, 2002
Room 208 (Hynes)

3:30 PM *C7.1
ADVANCED DYNAMIC SCANNING PROBES FOR THE CHARACTERIZATION OF SELF-ORGANIZED ORGANIC LAYERS. Harald Fuchs, Physikalisches Institut Westfälische Wilhelms-Universität Münster and Center for Nanotechnology (CeNTech), Münster, GERMANY.

Nanoscale Sciences are strongly driven by Scanned Probe Techniques which allow us to investigate and manipulate surfaces down to the atomic scale. While the imaging capabilities of techniques such as STM, SFM, SNOM etc. dominated the application of these methods at their early development stages, the physics of probe-sample interactions, and the quantitative analysis of elastic, electronic and magnetic surface and transport properties are becoming now of increasing interest. On recent progress in dynamic force microscopy/spectroscopy (SFM/SFS) as applied to polymers, and molecular layers such as OMBE-films and LB-films will be reported. In particular, Dynamic Force Spectroscopy (DFS) was introduced /1/ allowing us to understand quantitatively dissipative and non-dissipative processes in dynamic force microscopy /2/. Using a combined experimental and computer simulation technique it is possible reconstruct force/distance curves without using any model potentials and parameters. This method opens the perspective to extract material parameters such as atomic densities of the surface investigates as well as local elastic properties of the sample. In addition, energy dissipation occurring during high resolution imaging can be evaluated /3/. An instrumental improvement based on a modified electronic feed back control unit ('Q-control') allows us to effectively compensate for the hydrodynamic background damping that is sizeable for dynamic SFM operations in air and liquids. Effectively, the quality factor of the SFM cantilever beam can be increased, resulting in a sensitivity that is comparable to that of an SFM cantilever driven under vacuum conditions. Thus, soft organic materials such as organic layers and biological systems can be imaged without deterioration. This AFM-technique was applied to super molecular periodic layers /4/ and biological structures /5/. Scanning Near Field Optical Microscopy (SNOM) opens the perspective to apply optical imaging and spectroscopy techniques on soft matter far below the classical diffraction limit. On recent progress using a novel SNOM technique /6,7/ based on an aperture less probe exhibiting a lateral optical resolution of 1-10 nm will be reported. In the influence of the geometrical shape of a novel aperture like SNOM probe on its imaging properties of photonic nano structures will be discussed. References /1/ B. Gotsmann, H. Fuchs Dynamic Force Spectroscopy of Conservative and Dissipative Forces in an Al-Au(111) Tip-Sample System Phys. Rev. Lett. 86 (12), 2597-2600 (2001) /2/ B. Gotsmann, C. Seidel, B. Anczykowski, H. Fuchs Conservative and dissipative tip-sample interaction forces probed with dynamic AFM Phys. Rev. B 60, No. 15, 11051-11061 (1999) /3/ B. Anczykowski, B. Gotsmann, H. Fuchs, J.P. Cleveland, V.B. Elings How to measure energy dissipation in dynamic mode atomic force microscopy Appl. Surface Science 140, 376-382 (1999) /4/ M. Gleiche, L.F. Chi, H. Fuchs Nanoscopic channel lattices with controlled anisotropic wetting Nature 403, 173-175 (2000) /5/ Ch. M. Niemeyer, M. Adler, B. Pignataro, St. Lenhert, S. Gao, L.F. Chi, H. Fuchs, D. Blohm Self-assemply of DNA-streptavidin nanostructures and their use as reagents in immuno-PCR, Nucleic Acids Research 27, No. 23, 4553-4561 (1999) /6/ J. Koglin, U.C. Fischer, H. Fuchs Material Contrast in Scanning Near-Field Optical Microscopy (SNOM) at1-10 nm Resolution, Phys. Rev. B 55 (12), 7977-7984 (1997) /7/ C. Höppener, D. Molenda, H. Fuchs, A. Naber Simultaneous topographical and optical characterization of near-field optical aperture probes by way of imaging fluorescent nanospheres Appl. Phys. Lett. 80, 1331-1333 (2002).

4:00 PM *C7.2
POLYELECTROLYTE MULTILAYERS IN LIFE SCIENCE. Gero Decher, Univ Louis Pasteur, Institut Charles Sadron, Strasbourg, FRANCE.

Layer-by-layer (LBL) assembly (1) is an easy to use method for the fabrication of multi-composite films and has kindled widespread interest in such nanohybrids (1-7). Electrostatic interactions between anionic and cationic compounds (e. g. synthetic or natural polyions such as polyelectrolytes, DNA, proteins or even colloids) offer four major advantages: • layer-by-layer construction due to surface charge reversal in each layer • restriction to single layers due to repulsion between last layer and excess material • low steric demand for interaction between oppositely charged ions • deposition on almost any solvent accessible surface As an introduction to the (LBL) technique, the guiding principles of multilayer assembly will be presented and details of the film structure will be discussed. Since the technique allows to interface a wide variety of materials with predefined spatial arrangement, it has successfully been introduced to both materials science and applied bio-sciences. For this presentation we will focus on work in which individual layers are trapped in their respective position, on polyions which can diffuse and on films containing barriers layers. Furthermore we will dicuss the design of surfaces in contact with biological materials or environments. This will include work on films composed of natural or semi-synthetic polyions such as charged polypeptides or polysaccharides some of which has been carried out in close collaboration with the groups of P. Schaaf (ICS) and J.-C. Voegel (INSERM U 424). References to recent reviews: (1) Decher, G., Layered Nanoarchitectures via Directed Assembly of Anionic and Cationic Molecules; in: Comprehensive Supramolecular Chemistry, Vol. 9, "Templating, Self-Assembly and Self-Organization" (Sauvage, J.-P. and Hosseini, M.W., Eds.), Pergamon Press: Oxford, 1996; 507-528. (2) Knoll, W., Self-assembled microstructures at Interfaces. Curr. Opinion in Coll. & Interface Sci. 1996, 1, 137-143. (3) Decher, G., Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites. Science 1997, 277, 1232-1237. (4) Laschewsky, A., Ultrathin Polymer Coatings by Self-organization Techniques. Europ. Chem. Chronicle 1997, 2, 13-24. (5) Decher, G.; Eckle, M.; Schmitt, J.; Struth, B., Layer-by-Layer assembled multicomposite films. Curr. Opinion Coll. & Interf. Sci. 1998, 3, 32-39. (6) Bertrand, P.; Jonas, A.; Laschewsky, A. and Legras, R., Ultrathin polymer coatings by complexation of polyelectrolytes at interfaces: suitable materials, structure and properties. Macromol. Rapid. Commun. 2000, 21, 319-348. (7) Paula T. Hammond, Recent explorations in electrostatic multilayer thin film assembly. Curr. Opinion Coll. & Interf. Sci. 2000, 4, 430-442.

4:30 PM C7.3
MOLECULAR BIOMIMETICS: NEW STRATEGIES IN MOLECULARLY HYBRID MATERIALS. D. Heidel[a], S. Dincer[a], M. Duman[a], C. Nguyen, W-S. Choe, F. Baneyx, and Mehmet Sarikaya[a], [a]Materials Science and Engineering, and Chemical Engineering, University of Washington, Seattle, WA.

A common denominator in biological hard tissues (hybrids of organics and inorganics) is the presence of an organic phase, often in the form of mixtures of several proteins. The proteins allow collection of raw materials (bioinorganics), their transport, nucleation, growth and morphogenesis of hard tissues with intricate hierarchical structures that result in excellent physical properties, not encountered in synthetic systems. Mimicking biological materials (such as hard tissues) and biosystems (biomimetics) is one of the foci of future technologies for achieving complex architectures with predictable nanostructures. The key in molecular biomimetics is to use proteins as an integral component of the resultant hybrid materials system with significant addition to its physical and/or chemical structure or performance. Using combinatorial biological techniques, in particular, phage display and cell surface display technologies, we have developed protocols to select specific short polypeptides with high affinity to bind to useful inorganic surfaces. These genetically engineered proteins for inorganics (GEPI) are selected using, in particular, noble metals and semiconducting oxides with well-characterized surfaces. We will demonstrate that the GEPI can be used as molecular erector sets to assemble nanoparticles, to create biocompatible surfaces, and bridging molecules for nano-electronics and -photonics.

4:45 PM C7.4
SIMULATIONS OF CHIRAL LIQUID CRYSTAL SELF-ASSEMBLY: ANNALOGIES WITH THE STRUCTURAL FORMATION OF BIOLOGICAL FIBROUS COMPOSITES. Gino De Luca, Alejandro D. Rey, McGill University, Dept of Chemical Engineering, Montreal, QC, CANADA.

Nature produces composite materials with mechanical properties far beyond to those engineers are currently able to manufacture synthetically but still uses relatively simple constituents. The main reason for this is that the overall structural organization of natural composites is extremely hierarchical from the molecular to the submeter length scale. Beside their surprising mechanical properties, these materials are simultaneously adaptable and multifunctional. Moreover they also offer the attractions of biosynthesis,

biodegradability, and benign processing conditions. Thus, imitating some of the good practices of Nature can lead to enhancement of the design and the processing of synthetic engineering composites. A major research issue towards the development of such bio-inspired materials is the understanding of the microstructural behavior during the biological morphogenetic process. Biological composites are plywood-like laminated structures made of fibers. Because such precise three-dimensional arrangement requires a certain mobility of the fibers, it is strongly believed that the surrounding extracellular matrix passes through a liquid crystalline phase during development. Thus, the theories developed in condensed matter are potentially helpful to model and understand the formation process of biological fibrous composites. As handness is a rule in nature, biological fibrous composites naturally appear as analogues of chiral nematic liquid crystals. For mechanical reasons, the majority of the architectures found in biological fibrous composites are helicoidal monodomains, with layers arranged in planar or cylindrical fashion. In this work, the Landau-de Gennes phenomenological theory of chiral nematic liquid crystals is applied to numerically investigate the formation process of monodomain planar twisted architectures. Simulations provide qualitative explanations of the principles governing the formation process and the visualizations of the computed textures agree well with experimental observations. The highly non-linear mechanisms involved are described and characterized. Despite the simplifying assumptions used in the simulations, results confirm the relevance of liquid crystalline models in the study of biological fibrous composites structure formation.

SESSION C8: BIOMATERIALS - II
Chair: Dieter Fenske
Wednesday Morning, December 4, 2002
Room 208 (Hynes)

8:30 AM *C8.1
DEVELOPMENT OF A SYSTEM FOR EVALUATION OF ACCELERATED MICROBIAL BIODEGRADATION OF CEMENTITIOUS MIXTURES USED FOR IMMOBILIZATION OF LOW-LEVEL RADIOACTIVE WASTE. Alex Sivan, Orli Aviam, Merav Koresh, Ben Gurion Univ. of The Negev, Institute for Applied Biosciences, Beer Sheva, ISRAEL; Gabriela Bar-Nes, Yehuda Zeiri, Nuclear Research Center Negev, Dept. of Chemistry, Beer Sheva, ISRAEL.

Low level radioactive waste containing the short-lived isotopes Cesium and Strontium is usually disposed of (buried) following immobilization in concrete. It is important that the radioactive elements do not leach from the concrete to the soil for a period of 10 half-live, approximately 300 years. Consequently, there is a need to understand factors that affect concrete stability over long periods of time. Acid producing bacteria biodegrade concrete because the acid they release dissolves calcium minerals, weakening the concrete matrix. Sulfur oxidizing bacteria such as Thiobacillus spp. produce sulfuric acid, and are considered a primary agent of concrete biodegradation. A semi-continuous system for studying the biodegradation of concrete was developped. Biodegradation of various cementatious mixtures were examined in this system. Significant differences were observed between concrete samples that were incubated with the bacteria cultures and those of the control. After 30 days of incubation with the bacteria a weight loss of 9-12% from the concrete samples was obtained compared with almost no change in the weight of the control samples. Microscopic images of the concrete surface showed cracks caused by the acid secreted by the bacteria. The leaching of the various elements (Sr, Cs, Ca and Si) was greater in the presence of the bacteria and the kinetic of leaching, characterizing each element was revealed. A second system was developed which further accelerated the biodegradation rate of concrete during exposure to the acid-producing bacteria. The system operates continuously as a chemostat and exposes concrete samples to logarithmically growing cultures of bacteria in a medium containing thiosulfate as the sole energy source. Concrete biodegradation could be monitored by following weight loss as well as leaching of the ions mentioned above. The new system allows biodegradation kinetics to be determined in a period as short as two weeks.

9:00 AM C8.2
BIO-INSPIRED NANOSCALE POLYMER-CERAMIC HYBRID SYSTEMS. Ulrich Wiesner, Cornell University, Dept of Materials Science and Engineering, Ithaca, NY.

The study of amphiphilic polymer based functional polymer-ceramic 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 functional polymers as well as ceramic precursors unprecedented morphology control on the nanoscale is obtained. It is based on a unique polymer-ceramic interface. The hydrophilic parts of the polymer are completely integrated into the ceramic phase analogous to what is found in biological hybrid materials. Through this unique interface the ceramic phase is plasticized by the polymers thus leading to a novel class of materials referred to as "flexible ceramics". The structures generated on the nanoscale are a result of a fine balance of competing interactions, another feature of complex biological systems. A particularly fascinating structure discovered is a bicontinuous cubic morphology referred to as the "Plumber's Nightmare". This structure was known from surfactant studies but was not known to exist for polymers. The potential for new functional materials lies in the versatility of the sol-gel chemistry as well as that of the polymer chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructued materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. 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 as well as the synthesis of nanoobjects with controlled shape, size, and composition with potential biosensor applications. Reference: P.F.W. Simon, R. Ulrich, H.W. Spiess, U. Wiesner, Review: Block copolymer - ceramic hybrid materials from organically modified silicon precursors, Chem. Mater. 13, 3464-3486, (2001).

9:15 AM C8.3
CONTROLLED DRUG RELEASE FROM NANOSTRUCTURED SOL-GEL HYBRIDS. C.J. Barbe, R. Beyer and J.R. Bartlett, ANSTO, Menai, AUSTRALIA.

We present a generic approach to the synthesis of sol-gel silica matrices, with controlled nanostructures, for encapsulating bioactive drug molecules and controlling their subsequent release into aqueous media over periods ranging from hours to months. The bioactive species are incorporated into the matrix during gelation at, or near, ambient temperature. The internal nanostructure of the gels (pore volume, size and tortuosity, and surface chemistry), which controls the release kinetics of the bioactive species, can be precisely tailored by varying such sol-gel processing parameters as the water-to-alkoxide ratio, pH, alkoxide concentration, ageing, and drying conditions. Hence, the release rate of the encapsulated species is controlled by adapting the structure of the internal pore network to the physico-chemical properties of the bioactive molecule. Interactions between the matrix and the encapsulated species can be minimised by functionalisation of the internal surface. Combining emulsion synthesis with sol-gel technology enabled the carrier to be produced in the form of monodispersed, spherical particles, with internal nanostructures (and corresponding release characteristics) essentially identical to those of the equivalent bulk gels. The size of the monodisperse spheres (50 nm to 50 μm) was controlled by manipulating the hydrophile–lipophile balance between the surfactant, and aqueous and non-aqueous phases. As expected, the release rates increased monotonically with decreasing particle size, for equivalent sol-gel processing parameters. The ability to control the release kinetics of drugs encapsulated in such matrices by independently controlling the internal nanostructure and particle size renders this technology particularly attractive for therapeutical applications involving passive targeting of different internal organs.

9:30 AM *C8.4
Jim Heath, University of California-Los Angeles, CA. ♣

(ABSTRACT NOT AVAILABLE)

SESSION C9: PARTICLES - I
Chair: Dieter Fenske
Wednesday Morning, December 4, 2002
Room 208 (Hynes)

10:30 AM *C9.1
BIOLOGICAL APPLICATIONS OF NANOCRYSTALS. Paul Alivisatos, Univ of Calif, Dept of Chemistry, Berkeley, CA and Lawrence Berkeley National Lab, Berkeley, CA.

This talk will present recent work on shape control in semiconductor, metal, and oxide nanocrystals. Using "selective adhesion" of organic surfactants, we show a general approach to create rod and disk shaped nanocrystals. Work on using these nanocrystals to probe cell motility will be presented, as well as some recent advances on DNA conjugation and assembly.

11:00 AM *C9.2
DIAGNOSTIC DETECTION SYSTEMS BASED ON GOLD NANOPARTICLE PROBES. James Storhoff, Sudhakar Marla, Viswanadham Garimella, Uwe Muller, Tim Patno, Chris Khoury, Nanosphere Inc., Northbrook, IL.

Nanosphere's gold nanoparticle technology provides for remarkably sensitive and versatile label and detection systems for nucleic acid targets. The nanoparticles are coated with oligonucleotides in a proprietary process, which does not only confer chemical and thermal stability but additional unique properties. First, capture of nucleic acid targets on nanoparticles occurs under conditions of significantly elevated stringency and with extremely sharp melting transitions. Second, the coated particles are characterized by very low non-specific binding. The result is exceptional target specificity that allows highly reliable discrimination of single base changes for applications in SNP detection or genomic analyses. While the most simple detection strategies employ a color shift upon target mediated aggregation of the gold particles that can be observed with the unaided eye, a silver based amplification offers higher sensitivity and quantitation using simple and inexpensive light-scatter detection hardware. In that mode we have detected double-stranded DNA targets at 100 attomolar concentration (~600 copies total). Furthermore, the capture of target molecules in a narrow gap between two electrodes can be detected after binding of nanoparticles followed by silver deposition which results in conductivity changes that correlate with the quantity of captured target. The remarkable simplicity and sensitivity of nanoparticle based diagnostic systems lends itself to device miniaturization, and in many applications, to the reliable detection of targets without the need of target amplification.

11:30 AM C9.3
ODERING OF QUANTUM DOTS USING GENETICALLY ENGINEERED VIRUSES. Seung-Wuk Lee, Chuanbin Mao, Christine E. Flynn, and Angela M. Belcher, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX.

A liquid crystal system was used for the fabrication of a highly ordered composite material from genetically engineered M13 bacteriophage and zinc sulfide (ZnS) nanocrystals. The bacteriophage, which formed the basis of the self-ordering system, were selected to have a specific recognition moiety for ZnS crystal surfaces on their pIII proteins. The bacteriophage were coupled with ZnS solution precursors and spontaneously evolved a self-supporting hybrid film material that was ordered at the nanoscale and at the micrometer scale into ~72-micrometer periodic domains, which were continuous over a centimeter length scale. This periodic pattern strongly indicated that the M13 phage and ZnS nanocrystal hybrid film possessed a chiral smectic C structure, which comes from the chirality of M13 phage molecules. Our approach to aligning nanocrystals in a genetically-engineered phage-based liquid crystal system has several advantages. Monodisperse biopolymers of specified lengths (A7-phage) can be easily prepared by molecular cloning techniques. By genetic selection of a peptide recognition moiety, one can easily modulate and align different types of inorganic nanocrystals in 3D layered structures. We anticipate that our approach using recognition as well as a liquid crystalline self-ordering system of engineered viruses may provide new pathways to organize electronic, optical and magnetic materials.

11:45 AM C9.4
ASSEMBLY OF GOLD NANOPARTICLES ON DNA STRANDS. Michael Noyong, Kirsten Gloddek, Ulrich Simon, RWTH Aachen, Institute of Inorganic Chemistry, Aachen, GERMANY. ♣

Metallization of DNA has evolved to a great deal of interest from the scientific as well as from the technological point of view. Earlier works show the deposition of metal ions on micrometer long DNA strands from a metal salt solution followed by reduction [1-3].
In this work we report first results of a direct deposition from solution of surface modified 2nm Au nanoparticles onto DNA strands. In a two step protocol first cis-Pt (*cis*-Diamminedichloroplatinum(II), *cis*-$Pt(NH_3)_2Cl_2$) has been intercalated into the DNA duplex. In a second step cysteamine stabilized Au nanoparticles have been immobilized on the DNA due to a ligand exchange (NH_3 vs. NH_2-R) at the Pt center. The DNA/nanoparticle assemblies have been prepared on mica and silicon and are probed by AFM imaging. Structural features will be discussed.
[1] J. Richter, M. Mertig, W. Pompe, I. Münch, H.K. Schackert, Appl. Phys. Lett. **78**, 4, p. 536-538 (2001).
[2] W.E. Ford, O. Harnack, A. Yasuda, J.M. Wessels, Adv. Mater. **13**, 23, p. 1793-1797 (2001).
[3] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, Nature **391**, p. 775-778 (1998).

SESSION C10: PARTICLES - II
Chair: Steven M. Arrivo
Wednesday Afternoon, December 4, 2002
Room 208 (Hynes)

1:30 PM *C10.1
STRUCTURAL, THERMODYNAMIC AND OPTICAL PROPERTIES OF DNA-LINKED METAL NANOPARTICLE AGGREGATES AND ARRAYS: THEORETICAL STUDIES. George C. Schatz, Hai Long, Lin Lin Zhou and K. Lance Kelly, Northwestern Univ, Evanston, IL.

This paper describes our recent theoretical studies aimed at understanding two surprising properties of DNA-linked gold and silver nanoparticle aggegates and arrays. The first concerns the narrow melting transitions that have been found for both bulk aggregates and surface arrays. We present a theory of cooperative melting which successfully explains the data, including salt dependent melting effects. This theory attributes the sharp melting to multiple DNA's linking the nanoparticles, in combination with enhanced counterion condensation arising from sufficiently high density of oligonucleotides. The second property is concerned with recent observations of plasmon resonance spectra of planar nanoparticle arrays, where it has been found that the resonance wavelength blue shifts as density is increased for particles separated by 200-500 nm. Here we demonstrate that dipolar and higher multipolar coupling between particles lead to blue shifts when the particles are separated by sufficiently large distances that the radiative interactions dominate over static dipolar couplings. The static dipolar couplings produce red-shifted plasmons which dominate when the particles are closer than roughly 100 nm.

2:00 PM C10.2
THEORETICAL STUDY OF ELECTRON TRANSPORT THROUGH METALLIC NANOPARTICLES. Yongqiang Xue, Mark A. Ratner, Northwestern University, Department of Chemistry and Materials Research Center, Evanston, IL. ♣

Chemically-assembled nanoparticles represent an exciting new class of materials for both fundamental study of size- and shape-dependent properties of "artificial solid" and for novel applications in electronic, optoelectronic and biomedical devices. Electron transport process in this novel materials is governed by the interplay of tunneling, phonon-assisted hopping and single-electron charging effect which can be tuned separately by changing the nanoparticle size, the interparticle distance and the organic linker molecules used. In this work, we present a model calculation of electrical conduction through metallic nanoparticles where the energy quantization but not the charge quantization can be neglected. Both single nanoparticle and nanoparticle assemblies will be discussed. We examine the temperature and/or voltage dependence and the effect of nanoparticle size and interparticle distance on the conductance as transport through the barrier between neighboring nanoparticles or between electrode and nanoparticles changes from tunneling to thermal activation. The relevance of the theory to some recent experiments on molecularly-linked nanoparticles will also be discussed.

2:15 PM C10.3
FLUORESCENCE QUENCHING OF DYE MOLECULES NEAR GOLD NANOPARTICLES: RADIATIVE AND NON-RADIATIVE EFFECTS. E. Dulkeith, A.C. Morteani, T. Niedereichholz, T.A. Klar and J. Feldmann, Photonics and Optoelectronics Group, Physics Department and CeNS, University of Munich, GERMANY; S. Levi, F.C.J.M. van Veggel, D.N. Reinhoudt, Lab. for Supramolecular Chemistry and Technology, University of Twente, Enschede, THE NETHERLANDS; D.I. Gittins, Max-Planck-Institute of Colloids and Interfaces, Potsdam, GERMANY; M. Moeller, Dept. Org. Chemie III/Macromolekulare Chemie-OC III, Univ. of Ulm, GERMANY.

Resonant energy transfer (RET) systems consisting of organic dye molecules bound to gold nanoparticles play an important role in materials science as well as in biophotonics. After excitation of the molecule the energy can be transferred resonantly to the metal nanoparticle. Supplementary to this non-radiative decay process one has to consider the effect the nanoparticle exerts on the radiative rate of the dye molecule. We find that both processes play a crucial role in fluorescence quenching. Even for very small particles of 1 nm radius the fluorescence yield is reduced by 99.8% [1]. Time-resolved fluorescence experiments have been performed on donor-acceptor systems composed of lissamine dye molecules attached to gold nanoparticles. The distance between the chromophoric part of the molecules and the particle surface is 1 nm. The time constants for RET vary on a picosecond time scale and decrease when the particle radius is increased from 1 nm to 30 nm. In addition the dyes radiative rate turns out to decrease by more than an order of magnitude in the presence of the gold nanoparticles. Qualitative agreement of these drastic changes of the decay rates with the model proposed by Gersten and Nitzan is found. Quantitative discrepancies can be explained by non-local effects [1] E. Dulkeith, A.C. Morteani, T. Niedereichholz, T.A. Klar and J. Feldmann, S. Levi, F.C.J.M. van Veggel, D.N. Reinhoudt, M. Moeller, D.I. Gittins, submitted to Phys. Rev. Lett.

2:30 PM C10.4
SYNTHESIS OF COBALT NANOPARTICLES, NANORODS AND NANOWIRES ASSISTED BY OLEIC ACID AND OLEYLAMINE

BASED MIXTURES. 2D AND 3D ORGANIZATION.
Frederic Dumestre, Philippe Renaud, Digital DNA Labs, Semiconductor Products Sector, Motorola, Toulouse, FRANCE; Catherine Amiens, Bruno Chaudret, LCC-CNRS, Toulouse, FRANCE; Marie-Claire Fromen, Marie-Jose Casanove, CEMES-CNRS, Toulouse, FRANCE; Peter Zurcher, Digital DNA Labs, Semiconductor Products Sector, Motorola, AZ.

With the growing interest in building advanced materials with nanosized particles, there is a need for simple methods to control the shape and size of nanoparticles [1, 2, 3].
We report, here, a method of synthesis in solution of cobalt nanoparticles of various size and shape prepared from the decomposition of the organometallic precursor $Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})$ and stabilized by oleic acid / oleylamine amine based mixtures. Cobalt decomposition in the presence of a 1/1 mixture of oleic acid and oleylamine allows the formation of 3 nm spherical nanoparticles after three hours while generation of cobalt nanorods is observed when the reaction is continued for 2 days. We will also disscuss the possibility of varying the aspect ratio of the cobalt nanorods by using various combinations of acids and amines. For example, by using octadecyl-, hexadecyl-, dodecyl- and octylamine in association with oleic acid, it is possible to selectively produce nanorods of 6 x 47 nm, 5.5 x 120 nm, 8.2 x 33 nm, and 16.6 x 9.7 nm, respectively. An analogous control of the the nanorods aspect ratio can be achived by varying the acids alkyl chain length.
The nanoparticles obtained with oleylamine and oleic acid after three hours organized spontaneously on the TEM grid to produce super lattices with 1, 2 or more particles layers. The organization in solution or after deposition of the cobalt nanorods will also be presented and disscussed.
[1] Park, S-J. et al, *J. Am. Chem. Soc.* **2000**, 122, 8581.
[2] Puntes, V.F. et al., *Science* **2000**, 291, 2115.
[3] Cordente, N. et al, *Nano Lett.* **2001**, 1, 526.
[4] Weller D. and Moser A., *IEEE Trans. Magn.* **1999**, 35, 4423.

2:45 PM C10.5
TEMPERATURE PROGRAMMED ASSEMBLY OF METAL NANOPARTICLES. Glenn P. Goodrich, Mahnaz El-Kouedi, Christine D. Keating, The Pennsylvania State University, Dept of Chemistry, University Park, PA.

Metal nanoparticles show a great deal of promise as structural components in "bottom-up" assembly strategies for novel materials and devices. The optical and electronic properties of the metal nanoparticles, as well as their well-defined surface chemistries make them extremely well suited to molecular electronic and sensor applications. However, the challenge remains to direct nanoparticle assembly into functional structures. This work describes the use of DNA hybridization to direct particle assembly. Expanding on recent work involving DNA-modified noble metal nanoparticles, we are able to direct the assembly of particles based on the DNA sequences used and by controlling the temperature during assembly.

3:15 PM C10.6
BIO-INSPIRED DESIGN OF POLYMERS AS ANTIMICROBIAL PEPTIDE MIMICS. Gregory N. Tew and Lachelle Arnt, Department of Polymer Science and Engineering, University of Massachusetts-Amherst, Amherst, MA.

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 large scale. The design of polymers and oligomers that mimic the complex structures and remarkable biological properties of proteins is an important endeavor and would provide attractive alternatives to the difficult synthesis of natural peptides. We therefore have designed a series of facially amphiphilic arylamide polymers that capture the physical and biological properties of antimicrobial peptides, but are easy to prepare from inexpensive monomers. A number of different polymer backbones have been prepared including conjugated polymers like phenylene ethynylene. These polymers have good activity with minimal inhibitor concentrations in the low microgram per mL range. They are activity against a broad spectrum of bacteria including gram-postive and negative strains. Other experiments are discussed relating to the amphiphilic nature of the polymers.

3:30 PM C10.7
EXTERNAL CONTROL OF BIOMOLECULAR ACTIVITY VIA COVALENTLY ATTACHED NANOCRYSTAL ANTENNAS. Kim Hamad-Schifferli, Department of Mechanical Engineering, Joseph Jacobson, Media Lab; Jian Ping Shi, Shuguang Zhang, Center for Biomedical Engineering, MIT, Cambridge, MA.

Metal nanocrystals can be used as antennas for controlling the activity of biological systems. The authors present results in which the activity of DNA and proteins are controlled by covalently linked 1.4nm diameter Au nanocrystals. The nanocrystals are inductively heated by an alternating external magnetic field (frequency ~1GHz) that induces eddy currents in the nanocrystals. As a result, the nanocrystals transfer heat to the biomolecule to which they are attached. Induction heating of nanocrystals linked to DNA oligonucleotides in solution has been shown to dehybridize the DNA in a manner that is localized and reversible. Induction heating of antisense oligos appended with a nanocrystal is shown to turn off translation arrest, permitting translation. In addition, nanocrystals have also been attached to the enzyme Ribonuclease S, allowing specific and reversible control of the hydrolysis of RNA.

3:45 PM C10.8
HUMAN SPERMATOZOA ON NANOSTRUCUTURED Ag DEPOSITED ON GaAs SURFACE. Lucia G. Quagliano, Consiglio Nazionale delle Ricerche, CNR Institute for Nanostructured Materials, ISMN Area della Ricerca di Roma 1, Roma, ITALY.

Motivated by the SERS sensitivity to very small amounts of material we are interested in the application of the SERS technique for studying complex biological systems, such as cells. Surface Enhanced Raman Spectroscopy (SERS) is a very sensitive technique that employs rough substrates with structures in the nanometer range to enhance the Raman signal produced by adsorbed species. In SERS the effective Raman cross-section can be increased by many orders of magnitude. Using nanometer-size Ag particles deposited on GaAs surfaces as SERS-active substrates we have obtained an enhancement of Raman signal of human spermatozoa. In the presence of SERS-active substrate we have not observed any other significant spectral differences, indicating that there are not interaction of the cells with the surface. This is an important and crucial point concerning SERS studies of biological systems. It means that our SERS-active substrates serve only as amplifiers of Raman scattering and that the molecular structure of the cells is preserved after deposition on our SERS-active platform. In our opinion this kind of SERS-active substrates with nanometer-sized Ag particles on semiconductors might have promising application in nanoscale science and technology. In fact bio-molecules, cells and processes of their interfacing with Si, GaAs, silver and gold and other inorganic substrates, form the basis of bioelectronics a new emerging field at the crossing of molecular biology and nano-electronics with numerous electronic and biotechnological applications.

4:00 PM C10.9
COLLOIDS + DNA: FROM MORPHOLOGICAL DIVERSITY TO PROGRAMMABLE SELF-ASSEMBLY. Alexei V. Tkachenko, Department of Physics, University of Michigan, Ann Arbor, MI.

We study theoretically self-assembly of colloidal particles with DNA-mediated interactions. In this system, the sequence of ssDNA "markers" attached to a particle determines its type, and DNA "linkers" induce type-dependent interactions. Even in the simplest case of a binary mixture, the system is exhibits surprisingly diverse and unusual phase behaviour. Among the equilibrium morphologies are the diamond lattice, and the membrane phase with in-plane square order, a striking example of *spontaneous compactification*. We have also studied the possibility of "programmable" self-assembly of mesoscopic clusters of such particles with type-dependent interactions. This scheme is reminiscent of heteropolymer folding problem (e.g. RNA or protein). However, thanks to relatively long-range DNA-mediated interactions the system is capable of reaching its ground state directly, without being arrested at any metastable configuration.

4:15 PM C10.10
NANOSCALE PARTICLE ARRAYS INDUCED BY HIGHLY ORDERED PROTEIN ASSEMBLIES. Silke Behrens, Eckhard Dinjus, Forschungszentrum Karlsruhe, Institute of Technical Chemistry, GERMANY; Eberhard Unger, Institute of Molecular Biotechnology, Jena, GERMANY.

The use of biological molecules, assemblies and systems offers a variety of new synthetic methods for the development of interesting nano-scaled inorganic materials. These biotemplating methods take advantage of the characteristic nanometer dimensions of the biological specimen to built-up defined solid nanostructures. Inorganic systems with the patterns of the template will be available. In this paper, we report the formation and binding of nanometer-scaled noble metal particles on microtubules, that are highly ordered, cylindrical protein assemblies consisting of characteristically arranged α β heterodimeric tubulin subunits. The periodic functional groups of amino acids serve as active sites for nucleation and binding of the metallic nanoparticles

to form ordered chains and defined patterns of the particles and, by further particle growth, to form metallic nanowires with quasi-continuous metal coatings. The pattern of the nucleated nanoparticles reflects the regular arrangement of the tubulin molecules in the microtubule nanoparticle array.

4:30 PM C10.11
ENZYME-CONTAINING CARBON NANOTUBES FOR BIOCATALYTIC NANOMATERIALS. Dae-Yun Kim, Sandeep S. Karajanagi, Ravi S. Kane, Jonathan S. Dordick, Rensselaer Polytechnic Institute, Department of Chemical Engineering, Troy, NY; Nirapuma Chakrapani, Pulickel Ajayan, Rensselaer Polytechnic Institute, Department of Materials Science and Engineering, Troy, NY.

The ability to functionalize nanomaterials with biomolecules will be a key factor in determining how the promise of nanotechnology unfolds in the years to come. Biomolecules, by virtue of their unique selectivity, will not only be important in developing novel nanoarchitectures but will also play a critical role in imparting biological properties to the nanomaterials for their use in biological applications. Here we demonstrate the bioactivity of enzymes immobilized on single-walled carbon nanotubes (SWNTs) by covalent as well as non-covalent interactions. SWNTs were functionalized with 1-pyrene butanoic acid succinimidyl ester (P-NHS) by using non-covalent interactions. A protease, α-chymotrypsin, was then immobilized on the SWNTs by forming an amide bond with P-NHS. The amount of enzyme immobilized and its biocatalytic activity were determined. Higher enzyme loadings were obtained by adsorption on pristine bare SWNTs; however, the specific activity of the P-NHS functionalized tubes was about 3-fold higher than that of bare SWNTs. We have also incorporated a wide range of other proteins onto SWNT and MWNT, and their biocatalytic properties will be discussed. Finally, we have begun to develop biocatalytic architectures through highly selective affinity interactions between nanotubes and biospecific proteins, such as streptavidin. These biocatalytic architectures developed in this work have applications in novel anti-fouling, protein resistant coatings for biomedical applications, as well as aid in functionalizing the SWNT surface with active bio-based materials.

4:45 PM C10.12
STIMULI-RESPONSIVE NANOPARTICLES FOR CONTROLLED INSULIN DELIVERY. Todd C. Zion, Monica Sircar, Henry H. Tsang, Jackie Y. Ying, Massachusetts Institute of Technology, Cambridge, MA.

Polymer microencapsulation of proteins and other active substrates addresses several challenges in drug delivery such as (i) protection from harsh acidic and/or enzymatic environments, (ii) controlled release based on diffusion or polymer degradation, and in some cases (iii) targeting of agents to specific tissues based on particle size and/or surface chemistry. However, many clinical situations require drug release based on physiological needs rather than a constant rate, which has led to new developments in self-regulated drug delivery systems. Among these systems are hydrogels formed by multiple interactions between a protein and a polymer-bound biomolecule. The resulting materials degrade or swell in response to competitive binding of the free biomolecule. Our lab has recently developed a reverse-microemulsion mediated synthesis to formulate such materials into nanoparticles and applied the technique to the design of glucose-sensitive nanoparticles for controlled insulin delivery. This presentation will describe the novel design and synthesis of these polymer-protein hybrid nanoparticles, encapsulation of insulin, and glucose-stimulated release. In developing this technique, we have successfully addressed the challenge of stabilizing reverse-microemulsions in the presence of surface-active polymers and proteins. In addition, we have quantified the effects of these components on particle size using dynamic light scattering and electron microscopy. Finally, the concentrations of polymer, protein, and crosslinking agents have been optimized to provide maximum insulin encapsulation and adjustable glucose-sensitivity.

SESSION C11: POSTER SESSION
Chairs: Guenter Schmid and Ulrich Simon
Wednesday Evening, December 4, 2002
8:00 PM
Exhibition Hall D (Hynes)

C11.1
CONTROLLABLE FORMATION OF VIRAL ARRAYS USING DNA. Erica Strable[a,b], John E. Johnson[a], M.G. Finn[b], The Scripps Research Institute, [a]Department of Molecular Biology, [b]Department of Chemistry, La Jolla, CA.

At the root of many recent efforts in nanotechnology is the drive to create self-assembling systems from the atomic to the mesoscopic scale. Deoxyribonucleic acid is an attractive choice to control the assembly of supramolecular building blocks due to its high stability, inexpensive cost, and base-pairing specificity. Previous studies using DNA for generating arrays have been performed with gold nanoparticles and other amorphous supports. Here we describe the positionally-selective covalent attachment of organizing oligonucleotides to a virus, the structure of which is known to near atomic resolution. Cowpea Mosaic Virus (CPMV) is a readily-available plant virus that possesses an icosahedral protein shell composed of 60 copies of its coat protein. CPMV has been shown to have a single reactive lysine per subunit, and mutants of the virus have been made to insert a single exposed cysteine per subunit. We have taken advantage of these unique sites of reactivity to attach oligonucleotides to the virus surface. The derivatized particles display dramatic increases in retention time in anion exchange chromatography and have been characterized by a variety of techniques. Hexagonal arrays of CPMV particles can be generated my mixing populations of virus bearing complimentary oligonucleotide labels. Incubation of these arrays with an excess of competing complementary oligonucleotide results in the disassembly of the arrays, whereas a random sequence does not affect the arrays. Moving the position of the oligo on the capsid surface changes the appearance of the arrays, providing the first examples in this system of changing the properties of nanochemical aggregates by programming their building blocks.

C11.2
SCALED PRODUCTION OF NANOPARTICLES WITHIN PROTEIN TEMPLATES. R. Jones, D. Gleeson, A. Nartowski, B. Warne, K.K.W. Wong and E. Mayes, NanoMagnetics Ltd., Bristol, UNITED KINGDOM.

The regular manufacture of large quantities of nanoparticles is crucial for their uptake as commercial materials. In this paper we present the large-scale production of the empty iron-storage protein apoferritin and a subsequent reaction to form CoPt alloy nanoparticles within apoferritin. The scale-up of apoferritin production involves the replacement of the traditional method of using dialysis tubing which has limited production volume. The method we report on involves the use of ultrafiltration equipment based on pressure, as tangential ultrafilters result in poor product due to agglomeration. This process appears to scale from the current demineralisation of 16 g with moderate yields to kilogram quantities. We report on the synthetic procedure for the removal of native iron oxide, as well as quality assurance characterisations. Secondly we report on using the apoferritin product for the manufacture of CoPt alloy nanoparticles. The synthetic procedures and apparatus for production are discussed, and critical control parameters are highlighted.

C11.3
INTERACTIONS BETWEEN MAGNETIC NANOPARTICLES AND BIOLOGICAL CELLS: AN X-RAY SCATTERING STUDY. I. Koh, B. Cipriano, D. Williams, S. Ehrman, T. Pulliam-Holoman and L.J. Martinez-Miranda, Dept of Chemical Eng. and Dept of Materials and Nuclear Eng., University of Maryland, College Park, MD; S. Majetich, Dept. of Physics, Carnegie Mellon University, Pittsburgh, PA; G. Majetich, Dept. of Chemistry, University of Georgia, Athens, GA.

The study of the interaction of magnetic nanoparticles with cell membranes is of interest for drug delivery processes and for the development of additional medical diagnostic and treatment options. We have studied the structures formed by magnetic nanoparticles made of silicon oxide and iron oxide with cells to determine how they interact with the cells. Preliminary studies with E. coli have shown no toxicity effects and an increase in the magnetic response to fields higher than 350mT. For these fields a change in the layer spacing and in the intensity of the x-ray signal indicates a rotation with the magnetic nanoparticles. We combine the results of the x-ray study with fluorescent microscope observations to determine where the magnetic nanoparticles are located. Future studies will investigate the possibility of doing magnetoporation on cells. A phenomenum similar to magnetoporation has been observed in the so-called ferrosmectics.

C11.4
BIOINSPIRED IN SITU POLYMER HYDROXYAPATITE NANOCOMPOSITES FOR BONE REPLACEMENT. Kalpana Katti, Praveen Kumar Gujjula, Phanikumar Turlapati, Department of Civil Engineering, North Dakota State University, Fargo, ND.

Recently, in situ mineralization techniques have been utilized for development of hybrid nanocomposite systems for a variety of applications including biomedical. In situ mineralization of hydroxyapatite (HAP) in the presence of Ca binding polymers such polyacrylic acid has shown some promise towards improvement of mechanical response of uniaxial compressed HAP/polymer composites

to loading. This work represents fundamental studies on the nature of role of macromolecules on HAP precipitation and their impact on resulting bulk mechanical properties. Our results indicate that smaller plastic strains resulting in a superior recovery to loading cycles is exhibited by the in situ composites. XRD, SEM and FTIR microspectroscopic techniques are used to evaluate the crystal structure, crystallinity, microstructure and molecular structure of the in situ mineral and composites. This work also includes experimental studies on the response and molecular structure of the hybrid nanocomposites under simulated body fluid and aqueous environments. The control and development of molecular-level associations (as ascertained using photoacoustic FTIR) of polymer with HAP is suggested to be critical for the resulting macro mechanical properties. Our results may have significant implications in design of nanocomposites for biomedical applications.

C11.5
CONTROL OF INORGANIC MORPHOLOGIES BY ORGANIC TEMPLATES. Dorothy Duffy, John Harding, University College London, Dept of Physics and Astronomy, London, UNITED KINGDOM.

Biological organisms exhibit a remarkable ability to control the morphology and phase of inorganic crystals. Experiments have shown that ordered monolayers of large organic molecules can control crystal nucleation and growth. Calcium carbonate is a good candidate for study. It has three common phases and many candidate morphologies which are similar in energy. A wide variety of behaviour is therefore possible. The unrelaxed surfaces of the mineral and possible orderings of the functional groups in the film have been compared in simple epitaxial arguments to explain the behaviour. This ignores all effects of interface relaxation, surface electrostatics and hydrogen bonding. The critical quantity to calculate is the work of nucleation. This controls which morphology and phase appears. The interfaces between the monolayer and mineral and the interface between both these and water must be simulated. We have used molecular dynamics techniques to model these interfaces for stearic acid and a number of calcium carbonate surfaces. We find a strong interaction between the monolayer and the surface with a high degree of hydrogen bonding at the interface. For some orientations the surface structure was modified significantly by the monolayer. The calculated interfacial energy between monolayer and mineral is often high (of the order of 1 Jm^{-2}). This suggests that the nucleation rate will be strongly enhanced by the monolayers. We emphasise the importance of electrostatics when polar directions are considered. Such directions will be favoured when considering layers of stearate rather than stearic acid since the organic layer then forms the initial charged plane on which the polar direction is built. Space charge effects must also be considered in these situations. In the light of our results, we discuss when and if simple epitaxial arguments are a safe guide to predicting which morphologies and phases will be observed.

C11.6
AQUEOUS TWO PHASE SYSTEMS AS A TOOL FOR NANO-ASSEMBLY. Mahnaz El-Kouedi, Glenn P. Goodrich, Lisa M. Dillenback, Mark R. Etherton, Brian D. Reiss, Christine D. Keating, Pennsylvania State Univ, University Park, PA.

Aqueous two-phase systems (ATPS) have been utilized for years as a method for biological separations. Recently we have been developing techniques to use these systems to assemble metal nanowires into two dimensional raft structures at the interface formed between two polymers. Ultimately, these structures may be used as building blocks for new molecular electronic devices. Many properties of ATPS interfaces are particularly favorable for nanoparticle assembly techniques. The low surface tension at the interface provides a fluid, two-dimensional surface for assembly. Importantly, aqueous-aqueous systems are also biocompatible, allowing for the use of biomolecule linkers, such as proteins and DNA.

C11.7
NANOSTRUCTURED COMPOSITES AS CARTILAGE TISSUE ENGINEERING MATERIALS. Thomas J. Webster, Purdue University, Dept of Biomedical Engineering, West Lafayette, IN.

The objective of the present in vitro study was to determine functions of chondrocytes (cartilage-synthesizing cells) on polymer/nanophase ceramics that mimic the nanometer topography of cartilage tissue. Micron topographies of conventional poly-lactic/glycolic acid (PLGA) in composites were reduced into the biologically-inspired nanometer regime by soaking in various concentrations of NaOH solutions for select periods of time at room temperature. Nanophase or conventional, i.e. micron, grain size titania (Nanophase Technolgoies, Corp.) was incorporated at 30 wt.% in composites. Chondrocytes (Cell Applications, Inc.) were seeded (cell density of 3,500 cell/cm^2) in cell culture media and were allowed to proliferate on the substrates under standard cell culture conditions (that is, a humidified, 95% air / 5% CO2, 37°C environment) for 1, 3, and 5 days. After the prescribed time period, cells were fixed, stained, and counted. For long-term studies, chondrocytes were seeded (cell density of 40,000 cell/cm^2) in cell culture media and were cultured on the substrates under standard conditions for 7, 14, and 21 days. Total intracellular protein synthesis was examined after the prescribed time periods using the BCA Assay (Pierce) and gel electrophoresis. Experiments were run in triplicate and were repeated at three different times per substrate. Compared to conventional composites, chondrocyte proliferation was significantly higher on composites containing either nanostructured-PLGA or nanophase titania. Moreover, total intracellular protein synthesis was greater on composites containing either nanostructured PLGA or nanophase titania compared to conventional composites. Lastly, synthesis of chondrocyte expressed protein 68 (CEP-68; a protein indicating chondrocyte differentiation and synthesized exclusive by chondrocytes) was the highest on composites containing both nanostructured PLGA and nanophase titania. The present study, therefore, provides evidence that PLGA/titania composites which simulate the nanometer surface roughness created by proteins in soft tissues may enhance functions of chondrocytes necessary for successful regeneration of cartilage.

C11.8
ELECTRO-ACTIVATED THIOL-DISULFIDE EXCHANGE REACTION FOR SITE SPECIFIC IMMOBILIZATION OF BIOMOLECULES. Elisabeth Pavlovic, Sven Oscarsson, Center for Surface Biotechnology, Uppsala University, Uppsala, SWEDEN and Dept. of Chemical Engineering, Mälardalen University, Eskilstuna, SWEDEN; Arjan Quist, Center for Surface Biotechnology, Uppsala University, Uppsala, SWEDEN; Ulrik Gelius, Dept. of Physics, Uppsala University, Uppsala, SWEDEN.

A strategy for positioning and immobilization of biomolecules on surfaces has been investigated. The first step, the creation of a chemically reactive surface, consists of a new method for silanization of silicon oxide surfaces which enables the derivatization of the silicon surfaces with thiol terminated silane molecules. A dry argon flow was used to enhance the evaporation of thiolated silane molecules, therefore allowing these molecules to self-assemble on silicon oxide surfaces. Using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), it was shown that the silane coverage is a tightly packed monolayer with a surface roughness as low as 0.19 nm. The second step is the activation of surface thiols by generating thiolsulfinates/thiolsulfonates that display a high reactivity toward free thiols, resulting in a disulfide exchange. This is done by applying a voltage between a cupper cathode and a thiol derivatized surface as the anode, in a buffer solution. Cyclic voltammetry experiments indicated that the oxidation of thiols is performed via the oxygen produced by electrolysis of water. XPS data showed the amount of thiolsulfinates/thiolsulfonates was dependent on the voltage applied. Peptides containing thiol groups were subsequently covalently bound to the surface through disulfide bonds. It was possible to break the disulfide bonds with dithiothreitol (DTT) and release the peptides from the surface. The final step will be to use nanosized electrodes or an AFM tip as counter-electrode to achieve a spatially controlled immobilization of biomolecules on surfaces at the nanometer scale.

C11.9
SCALE-UP STUDIES FOR THE UNRAVELING OF COLLAGEN BUNDLES. Mary Ann Seltzer, Joseph Mulato, Gennaro Maffia, Department of Chemical Engineering, Widener University, Chester, PA.

Dispersions made from insoluble collagen fibrils have demonstrated efficacy in such diverse fields as sludge settling and the manufacture of porous substrates for cell growth. The key to all of the collagen-based technologies is the ability of the isolated collagen fibril, with surface area greater than 30 m2/g, to retain hundreds of times its mass in water. Collagen fibrils, of 100 nm diameter, are isolated from bovine corium is a multi-step process that involves non-destructive milling and centrifugation. Current production techniques are long and labor intensive. Scale-up issues are being addressed using larger mills, chemical pretreatment, and sonication. Results are presented from analyses performed using SEM and AFM, as well as physical testing techniques; such as, DSC, electrophoresis, rheology, and swelling ratio.

C11.10
DEVELOPMENT OF RADIOACTIVE DENDRIMER NANOCOMPOSITE DEVICES FOR IMAGING AND RADIOTHERAPY OF TUMORS. L. Balogh, A.C. Cook, Shraddha Nigavekar, and M.K. Khan, University of Michigan, Ann Arbor, MI.

We report on the fabrication and development of radioactive nanocomposite devices (NCDs) to deliver radioisotopes to tumors by exploiting differences between normal and tumor vasculature. Our study (DOE No.: FG01-00NE22943) presently focuses on the development of Au-198 nanocomposites to delive beta-radiation to

tumors in a B16 melanoma bearing mice model. These water-soluble non-toxic NCDs are synthesized as monodisperse and stable hybrid nanoparticles composed of poly(amidoamine) (PAMAM) dendrimers and gold atoms as guests. Au(0) atoms were made radioactive either before or after particle fabrication by direct irradiation in a neutron beam making both imaging and radiotherapy possible. In addition to other radiochemical methods, it is easy to observe and identify gold NCD particles in tissues or cells by transmission electron microscopy as no other objects can be found in tissues or cells that are similar in shape, size and contrast to the nanocomposite cluster devices. These NCDs can have a specific charge, content and adherence to cells and therefore may also be used to map certain cell compartments and cellular structures. This technique enables us to first synthesize the nanomaterials, then fabricate and characterize the complex device, and finally activate the NCDs. This approach will shorten the develop-ment of new active NCD systems allowing the use of other short half-life radionuclides as well.

C11.11
ENGINEERED FILMS OF *BOMBYX MORI* SILK WITH POLY(ETHYLENE OXIDE). Hyoung-Joon Jin, Jaehyung Park, David L. Kaplan, Tufts University, Department of Chemical & Biological Engineering, Bioengineering Center, Medford, MA; Peggy Cebe, Tufts University, Department of Physics and Astronomy, Medford, MA.

Solution processing was used to incorporate water-soluble polymers such as poly(ethylene glycol) (3,400 g/mol) or poly(ethylene oxide) (900,000 g/mol) into *Bombyx mori* silkworm silk fibroin to improve processability, mechanical properties and surface hydrophilicity. The presence of the PEG or PEO on the blend surfaces was verified by contact angle and XPS. The compatibility between the two polymers (silk/PEG and silk/PEO) was assessed by DSC and SEM and micro and macro phase separation was characterized by WAXD and SAXS using Synchrotron. From SEM images of blend films a unique morphology was observed in which the sizes of the silk phase globules could be manipulated based on the content of PEO. DSC analysis also confirmed some interactions between the two polymers.

C11.12
HUMAN BONE MARROW STEM CELL RESPONSES ON ELECTROSPUN *BOMBYX MORI* SILK FIBROIN. Hyoung-Joon Jin, Jingsong Chen, Vassilis Karageorgiou, Gregory H. Altman, David L. Kaplan, Tufts University, Department of Chemical & Biological Engineering, Bioengineering Center, Medford, MA.

Electrospinning for the formation of nanoscale diameter fibers has been explored for high performance filters and biomaterial scaffolds for vascular grafts or wound dressings. Fibers with nanoscale diameters provide benefits due to high surface area. In this study we used electrospinning for protein-based biomaterials to fabricate scaffolds from aqueous regenerated silkworm silk, *Bombyx mori*, solutions. Adhesion, spreading, proliferation, and collagen matrix production of human bone marrow stem cells (hBMSCs) on electrospun silk was characterized. Scanning electron microscopy (SEM) and MTT analyses demonstrated that the electrospun silk matrices promoted hBMSC attachment and proliferation over 10 days in culture when compared with native silk fiber matrices. The responses of the hBMSCs on the electrospun silk matrices, combined with the biocompatibile properties of the silk fibroin protein matrix, suggest potential for use of this biomaterial as scaffolds for tissue engineering.

C11.13
Abstract Withdrawn.

C11.14
Abstract Withdrawn.

C11.15
VIRUS-DERIVED ARCHITECTURAL LATTICEWORK NANOCOMPONENTS. Edward Goldberg, Tufts University, Department of Molecular Biology and Microbiology, Boston, MA; Paul Hyman, NanoFrames LLC, Boston, MA; Regina Valluzzi, Tufts University, Department of Chemical and Biological Engineering/ Bioengineering Center, Medford, MA.

Bacteriophage T4 is a virus consisting of a head, a tail and tail fibers extending from the tail which attach and hold the virus to a host bacterium. The tail fibers consist mainly of a beta sheet secondary structure which makes them extremely stiff and strong relative to other proteins, and suggests a high thermal and chemical stability in the solid state. The component proteins which make up the tail fiber have well-defined domains for assembly and attachment. These domains can be rearranged and added to, to make fibers with novel properties. The native tail fibers are 160 nm long and 3 nm wide, allowing their use in designed nanoarchitectures with features at comparable length-scales. Living cells normally assemble mesoscale structures (e.g. muscle fibers, mitotic spindles, flagella, virus particles) following well-studied mechanisms including vectorial assembly and specific interaction moieties. Our approach is to create a set of nanoscale subunits of precise size, shape and functionality that can be assembled in a similar massively parallel manner. The tail fiber proteins of bacteriophage T4 make up a self-assembling, precisely defined, highly stable structure and, as we will show, are readily amenable to re-engineering without losing these properties. These features, along with a facile route to sequence and structure engineering, make tail fibers attractive as struts to construct unique self-assembled open architecture meshes in two and three dimensions. Recent results pertinent to re-engineering, processing, self-assembly (into patterned nanomaterials) and characterization of tail fiber based aggregate (self-assembled) materials will be presented.

C11.16
Abstract Withdrawn.

C11.17
ELECTRIC FIELD AND CHARGED MOLECULES MEDIATED SELF ASSEMBLY FOR ELECTRONIC DEVICES. S.W. Lee, H. Mcnally, R. Bashir, Purdue Univ, School of Electrical and Computer Engineering, West Lafayette, IN; M. Pingle, D. Bergstorm, Purdue Univ, Department of Medicinal Chemistry, West Lafayette, IN. ♣

The integration of nano- and micro-scale heterogeneous materials is very important for electrical, optical, and sensing application using bio-inspired self-assembly. However, challenges such as yield of assembly, controllability of position, and efficiency of self-assembly still remain in order to implement useful electronic device for the construction of the complex system. In this paper, we present a process to fabricate, charge, and release silicon electronic devices from a SOI wafer. The devices are fabricated with a gold layer, on which a 2-mercaptoethansulfonic acid sodium salt, a single stranded DNA, or an acetylthiocholine iodide is attached using an S-Au (thiolate) covalent bond. Those molecules provide negative or positive charges into the silicon devices and hence devices with these charged molecules can be simultaneously moved to different sites. The devices are then released in a low conductivity buffer using an ultrasonic frequency-mediated release process. Subsequently, those charged devices are selectively assembled into proper binding cites on silicon or other substrate by electric field. Electrical properties of these devices including resistors and junction diodes is investigated after the assembly has occurred. The technique described can be used to integrate the hybrid device such as nano- or micro-scale resistors, PN diodes, and MOSFETs on silicon or other substrates such as glass, plastic, etc. Furthermore, it can be applied for the construction of flexible displays and the integration of electronic elements such as memory, display, and sensors on the same substrate.

C11.18
COMPARISON WITH AMINO GROUP AND HYDROPHILIC GROUP FOR PROTEIN AFFINITY BY EXCIMER LASER INDUCED FUNCTIONAL GROUPS SUBSTITUTION ONTO PET FILM. Hitoshi Omuro, Masato Nakagawa[a], Hiroaki Fukuda[b] and Masataka Murahara, Department of Electrical Engineering, Tokai Univ, Hiratuka, Kanagawa, JAPAN; [a]Mizue Clinic, Edogawa, Tokyo, JAPAN; [b]Saiseikai Hiratuka Hospital, Hiratuka, Kanagawa, JAPAN.

Amino functional group(NH_2) and hydrophilic group(OH) were substituted on a PET film surface. PET has been widely used for medical materials such as an artificial ligament. However, the affinity of tissues is no good. To compensate this, the mesh formed PET was used for artificial ligament intruding tissue into mesh clinically. However, this method has not shown sufficient affinity with the tissue, thus an initial adapting power of material and tissue is weak. "Biocompatibility is necessary for the artificial ligament that contacts blood and tissues. However the foregoing artificial ligament doesn't satisfy the biocompatibility." Then we substituted NH2 and OH functional groups, which has a high affinity with tissue on the PET surface. Firstly, an ArF excimer laser beam was irradiated onto PET in water. And this photochemical reaction OH functional group was substituted on PET surface. Secondly, the ArF excimer laser beam was irradiated onto PET in ammonia gas. And this photochemical reaction NH_2 functional group was substituted on the PET surface. By these experimental results, untreated sample has the contact angle of 80 degrees with water, and the bonding strength with protein is only 1.0kg/cm^2. In case of the modified sample with water, the contact angle was improved to be 30 degrees, and the bonding strength to be 10kg/cm2. When treated in ammonia gas, the contact angle was improved to be 30 degrees, however the bonding strength was almost the same as the untreated sample. Then, the fibroblast was cultivated on the sample. It was confirmed that the number of the fibroblast was in accord with the value of contact angle with water. By the increasing or decreasing of the substitution concentration of OH and NH_2 functional groups on the PET surface, it is considered that the affinity of the PET for water and protein can be controlled.

C11.19
STABILIZATION OF GOLD NANOCRYSTALS BY ORGANIC DENDRON LIGANDS. J. Jack Li, Y. Andrew Wang, Xiaogang Peng, Univ of Arkansas, Fayetteville, AR.

Stability of gold nanocrystals in surface modification process and thereafter in biochemical applications is an outstanding issue. Au nanocrystals are often being precipitated in the highly ionic environments associated with these processes because of the insufficient protection from the ligand layer or the ligand loss due to photooxdation. With organic dendron ligands designed and synthesized in this lab we demonstrated that the dendron ligand modified Au nanocrystals can withstand the harsh conditions in ligand coupling reaction and in biochemical applications in the contrast to the single chained hydrophilic organic thiols. Furthermore the intrabranch tangling of the organic dendron ligands may prevent the biomolecules (e.g. DNA) linked ligands from being lost from the gold nanocrystals, which may cause signal loss in the DNA detection where the gold nanocrystals act as the reporters.

C11.20
PREPARATION AND CHARACTERIZATION OF MESO-STRUCTURED POROUS SILICA FILMS WITH CLOSED CELLS. Kui Yu, National Research Council Canada, Steacie Institute for Molecular Sciences, Ottawa, CANADA; C. Jeffrey Brinker, Sandia National Laboratories, Albuquerque, NM; Bernd Smarsly, Univ. of New Mexico, Center for Micro-Engineered Materials, Albuquerque, NM.

Mesostructured silica/diblock thin films with a 3D arrangement of spherical domains (bcc) were prepared through evaporation-induced self-assembly (EISA). The silica precursors used were MTES (Si(OCH2CH3)3CH3) and/or TEOS (Si(OCH2CH3)4); the structure-directing agents used were polystyrene-block-poly(ethylene oxide) (PS-b-PEO) diblock copolymers. The meso- and micro-structures was cautiously investigated by transmission electron microscopy (TEM) and 2D Grazing Incidence Small Angle X-Ray Scattering (GISAXS). A novel method, so-called "chord-length distribution" (CLD), was used to quantitatively evaluate the SAXS data for the microstructure. The present study suggests that the mesoporous calcined silica films consist of isolated voids with a cubic array (bcc) and no significant degree of additional microporosity is present. According to the CLD calculation, the average distance between the methyl ligands on the calined film is ca. 1-1.4 nm, depending on the MTES content in the silica precursor. Therefore, it is promising to tune the hydrophobicity of calcined mesostructured porous silica films via using mixtures of TEOS and MTES as silica precursors, due to no significant disappearance of the methyl ligand after calcination and the random copolymerization of MTES and TEOS. The present prepared mesostructured porous silica thin films are believed to be the first to consist of isolated voids with a 3D array distributed in an inorganic matrix without additional microporosity, and to be the first to use MTES as the silica precursor. Such closed-cell mesostructured porous silica thin films with high porosity and controllable hydrophobicity can be excellent candidates for low dielectric (k) insulator materials.

C11.21
DNA-MEDIATED ASSEMBLY OF BIDISPERSE, MICRON-SIZED COLLOIDS. Valeria T. Milam, Amy Hiddessen, Daniel A. Hammer, Dept of Bioengineering, University of Pennsylvania, Philadelphia, PA; John C. Crocker, David J. Graves, Dept of Chemical Engineering, University of Pennsylvania, Philadelphia, PA.

We have studied DNA-mediated assembly of micron-sized, bidisperse mixtures using primarily optical and confocal microscopy. Unlike most bioadhesion molecules which bind together with high affinity, the attraction between complementary DNA strands can vary greatly depending on strand characteristics (e.g. length, sequence choice) and solution conditions (e.g. ionic strength, temperature). In order to increase hybridization efficiency between complementary strands, DNA sequences in this study were designed by J. Crocker to have low self-affinity to minimize loop and hairpin formations. Single strands of biotinylated DNA were tethered to avidin-coated 0.95 and 1.87 micron beads. The resulting oligonucleotide density on the bead surface was checked using flow cytometry. After mixing, we observed a range in the degree of attraction between heterogeneous beads depending on the solution ionic strength and temperature. We have also observed a variey of colloidal structures such as chains of alternating large and small particles by exploring additional experimental variables such as particle number ratio and volume fraction.

C11.22
FRACTURE AND FATIGUE BEHAVIOR OF A SELF-HEALING POLYMER COMPOSITE. Eric N. Brown, Nancy R. Sottos[a], Dept of Theoretical & Applied Mechanics, Urbana, IL; Scott R. White[a], Dept of Aerospace Engineering, Urbana, IL; Jeffrey S. Moore[a], Dept of Chemistry, Urbana, IL. [a]authors affiliated with the Beckman Institute for Advanced Science and Technology, Urbana, IL.

Inspired by biological systems, in which damage triggers an autonomous healing response, a polymer composite material that can heal itself when cracked has been developed. The material consists of an epoxy matrix composite, which utilizes embedded microcapsules to store a healing agent and an embedded catalyst. This paper investigates issues of fracture and fatigue consequential to the development and optimization of this new class of materials. When damage occurs, the propagating crack ruptures the microcapsules, which then releases the healing agent into the crack plane. Polymerization of the healing agent is triggered by contact with the exposed catalyst, which bonds the crack faces closed. The efficiency of crack healing is defined based on the ability of a healed sample to recover fracture toughness. Healing efficiencies of over 90% have been demonstrated.
Under monotonic loading, the addition of urea-formaldehyde microcapsules with 150 to 250 nm shell wall thickness, is shown to significantly increase epoxy fracture toughness. The extent of toughening is dependent on the microcapsule concentration and size, and is shown to result from a change in the fracture mechanism of the matrix. Fracture surfaces on both virgin and healed fracture specimens are examined using electron microscopy. Without microcapsules, the neat epoxy exhibits a cleavagelike brittle fracture. The addition of microcapsules induces localized toughening evidenced by the presence of hackle markings across the entire fracture surface. Fatigue crack propagation, even in a tension-tension mode, may reveal significantly different features from those under monotonic loading. Prior fatigue studies of particulate reinforced epoxies indicate that local crack-tip shielding mechanisms are invoked only above a certain threshold of stress intensity range. Currently investigations in our laboratory are focused on characterizing the fatigue behavior of self-healing epoxy.

C11.23
MOLECULAR WEIGHT DEPENDENCE OF POLYMERSOME MEMBRANE STRUCTURE, ELASTICITY, AND STABILITY. Harry Bermudez[a], Aaron K. Brannan[b], Frank S. Bates[b], Daniel A. Hammer[a], Dennis E. Discher[a]; [a]School of Engineering and Applied Science, University of Pennsylvania, Philadelphia, PA; [b]Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Vesicles prepared in water from a series of diblock copolymers - "polymersomes" - are physically characterized. With increasing molecular weight $\bar{M}_n$, the hydrophobic core thickness d for the self-assembled bilayers of poly(ethylene oxide)-polybutadiene (PEO-PBD) increases up to ~20 nm; which is considerably greater than any previously studied lipid or polymeric system. The mechanical responses of these membranes, specifically, the area elastic modulus K_a and maximal areal strain α_c are measured by micromanipulation. As expected for interface-dominated elasticity, K_a (~100 dynes/cm) is found to be independent of $\bar{M}_n$. Furthermore, α_c increases with $\bar{M}_n$, approaching a limiting value predicted by mean-field ideas which is universal and about ten-fold above the typical value for lipids. Nonlinear responses and memory effects generally emerge with increasing $\bar{M}_n$, indicating the onset of chain entanglements at higher $\bar{M}_n$. The results highlight the interfacial limits of self-assemblies at the nanoscale.

C11.24
MECHANICS OF PROTEIN ASSEMBLIES IN BACTERIOPHAGE T4. Wayne M. Falk and Richard D. James, Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN.

Bacteriophage T4 is a common virus that may give insight into designing materials that produce motion and force at small scales. During infection, the virus' tail contracts, puncturing the bacterial host's cell wall without any external input of energy. The proteins forming the tail sheath supply the energy by changing their conformation and collective bonding arrangement. Contraction of the tail sheath occurs as a wave that travels upwards transforming the protein lattice while maintaining all major protein-protein bonds. This is similar to the displacive phase transition occurring in shape memory alloys. Using concepts from the mechanics of phase transformations, we formulate a predictive, quantitative theory for this material. The proteins which make up the virus' tail are globular which allows us to describe the kinematics of each protein with a single position and orientation. We can represent the bonding energy of each molecule with an unknown function of the relative positions and orientations of the proteins. Based on these kinematics and the observed behavior of the sheath, we derive necessary properties for three regions of the energy: (1) the metastable extended phase, (2) the stable contracted phase and (3) the interfacial energy barrier

which divide them. These properties are used to deduce a kinetic equation for the force of contraction.

C11.25
ORGANIC/INORGANIC HYBRID NANO- AND MICRO-COMPOSITES OF POLYANILINE AND METAL OXIDES. Yue Ma, Kaiguo Chang, Hui Wan, Zhexiong Tang, Sze C. Yang, Dept of Chemistry, University of Rhode Island, Kingston, RI; John Sinko, Wayne Pigment Corp., Milwaukee, WI.

Organic / Inorganic hybrid micro and nano composites were prepared and studied. The inorganic components of the hybrid are metal oxides including titanium dioxide, zinc oxide, silica, molybdenum oxide, vanadium oxide, and zirconium hydrogen phosphate and tungsten oxide. The organic components are polymeric complexes of polyaniline and polypyrrole. The polymeric complexes were synthesized by a template-guided synthetic strategy to form a double-strand polymer with the first strand being a p-conjugated polymer and the second strand being a polyelectrolyte. Examples of the second strand are poly(acrylic acid) and poly(vinyl yl ether / monoethyl maleate). The process for hybrid preparation and the properties of the hybrid material will be reported. The stability and the potential synergy between the conducting polymer and the inorganic component for applications will be examined.

C11.26
HOLLOW SHELLS OF EXFOLIATED TITANIA NANOSHEETS FABRICATING BY LAYER-BY-LAYER ASSEMBLY ON POLYMER TEMPLATES. Lianzhou Wang, Takayoshi Sasaki, Yasuo Ebina, and Mamoru Watanabe, Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, JAPAN.

Hollow spheres with nanometer-to-micrometer dimensions have attracted considerable attention because of their potential application as photonic crystals, catalysts, delivery vehicles, etc. Some procedures have been developed to fabricate hollow spheres of metals, polymers and inorganic materials using template-assisted approaches. Recently, the layer-by-layer self-assembly approach has been applied to the formation of core-shell composites, and subsequent conversion resulting to hollow spheres. To date, one of the main challenges for this pathway is to produce uniform and controllable structures of shells. Here we report the titania hollow spheres with controlled thicknesses and uniform structures. The fabrication is involved stepwise adsorption of polycations and exfoliated titania nanosheets onto polymer spheres, and subsequent heat- or UV-treatment to remove the templates. The flexible unilamellar titania nanosheets (200 $\sim$ 400 nm; ca. 0.75 nm in thickness) can behave as some "wrapping papers" to produce the reliable replica of original template morphologies. Scanning electron micrographs revealed that the core-shell composites with uniform coatings in the range from 0.4 micrometer to 10 micrometer could be readily obtained. XRD and TG-DTA analysis indicated the regular growth of titania shells on the templates with increasing coating cycles. Transmission electron micrographs showed that the wall thickness of the hollow spheres could be precisely controlled by varying the number of coating cycles. Extremely thin hollow spheres (4 $\sim$ 5 nm in thickness) with smooth curvatures could be obtained after 5 coating cycles, indicating the feasibility of our synthetic procedure in fabricating ultrathin spheres. The resulting titania hollow shells exhibited various optical properties, depending on the treatments, which may find applications in photochemical fields.

C11.27
NEPHELOMETRIC DETECTION OF SINGLE NUCLEOTIDE DIFFERENCE BASED ON SALTING-OUT TECHNIQUES WITH DNA-CARRYING COLLOIDAL NANOPARTICLES. Tohru Takarada, Zhonglan Tang, Mizuo Maeda, Kyushu Univ, Dept of Applied Chemistry, Fukuoka, JAPAN and RIKEN, Bioengineering Lab, Wako, JAPAN.

A single nucleotide mutation on certain genes can cause heritable disorders and cancers. Accordingly, the development of a simple and practical detection method for single nucleotide difference has been one of the most important subjects in analytical biochemistry. Recently, Mirkin and co-workers have successfully demonstrated that DNA-linked gold nanoparticle probes are applicable for such differentiation. Their detection method is based on a red shift in the surface plasmon resonance of the gold nanoparticles cross-linked through hybridization with target single-stranded DNA. In this study, we applied a salt concentration-dependent turbidity change of colloidal particle dispersion to a single-base difference assay. The colloidal nanoparticle comprises a hydrophobic core of poly(*N*-isopropylacrylamide) (polyNIPAAm) and a hydrophilic shell of oligonucleotide (ODN) strands. The particle was constructed by self-assembly of amphiphilic random copolymers of ODN derivative and NIPAAm. When an aqueous solution of the copolymer was incubated above the phase transition temperature of polyNIPAAm, the colloidal nanoparticle formed spontaneously and kept dispersing. In the presence of an adequate amount of NaCl, the nanoparticles aggregated rapidly when the complementary ODN was added into the dispersion and hybridized to the probe ODN fixed on the surface of the particle. In contrast, the colloidal nanoparticle kept dispersing with any point-mutated ODN under the identical conditions. These distinct phenomena should be applied for a facile point-mutation assay in gene diagnosis.

C11.28
LASER-INDUCED PHOTOCHEMICAL SURFACE MODIFICATION OF INTRAOCULAR LENS FOR BLOCKING AFTER-CATARACT. Katsuya Tanizawa, Yuji Sato, Masataka Murahara, Tokai Univ, Dept of Electrical Engineering, Kanagawa, JAPAN; Jean Marie Parel, Univ of Miami School of Medicine, Bascom Palmer Eye Institute, Miami, FL.

The central part of PMMA lens was modified to be hydrophobic and the peripheral part to be hydrophilic by photochemical reaction with ArF excimer laser and chemicals. PMMA has a high-transmittance property in the visible light and has been used as an intraocular lens. However, protein and fat are stuck onto the lens surface after a long-term insertion and cause the surface get opaque; that is the after-cataract. Accordingly, the central part of the lens was modified to be hydrophobic in order to protect the PMMA lens from fat and protein. And, the peripheral part was modified to be hydrophilic to develop an affinity for the tissue. Firstly, ArF laser (147kcal/mol) irradiated the central part of a lens in the presence of fluorine oil (perfluoropolyether) or CF_n gas ambience. By this photochemical reaction, the CF_3 functional group was substituted on the PMMA surface. Secondly, ArF laser (147kcal/mol) irradiated the peripheral part of a lens in the presence of water. By this photochemical reaction, the OH functional group was substituted on the PMMA. The contact angle with the physiological salt solution was measured. The contact angle of the non-treatment sample was 83 degrees. The one treated with perfluoropolyether was 105 degrees at the laser shot number of 2000 with the laser fluence of 15(mJ/cm^2). When using $CBrF_3$ and $CClF_3$, the contact angles were both 91 degrees at the laser shot number of 5 with the laser fluence of 20(mJ/cm^2). And, the one using the water was 30 degrees, less than the contact angle of the non-treatment sample. It was confirmed that the exposure part of the PMMA surface with laser was modified into hydrophobic or hydrophilic by the existence of oil and water. In conclusion, our study demonstrated the production of the ideal intraocular lens.

C11.29
SCAFFOLDING FOR THE RE-GROWTH OF BONE TISSUE DEVELOPED FROM A HYDROXYAPATITE/ POLYCAPROLACTONE COMPOSITE. S. Iadarola[a], A. Crugnola[b], R. Joshi[b], J. Tessier[c], B. Kang[a], S. Farboodmanesh[d], and C. Sung[a]; [a]Department of Chemical and Nuclear Engineering, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA; [b]Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, MA; [c]Department of Clinical Science, University of Massachusetts Lowell, Lowell, MA; [d]Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, MA.

The goal of this project is to develop scaffolding from a blend of hydroxyapatite powder and polycaprolactone and to determine bone cell viability within the scaffolding. Hydroxyapatite (HA), a mineral found in natural bone, is an osteoconductive material that has shown excellent biocompatibility and the ability to form chemical bonds with natural bone. Polycaprolactone (PCL) is a biocompatible polymer that is also biodegradable/bioresorbable. The scaffolding will be characterized by SEM and TEM. Following osteoblast cell growth, SEM will be used determine the extent of penetration and cell viability within the scaffolding. If successful in this project, the scaffolding would serve as a device to re-grow bone within the body. The scaffolding specimens were formed by two techniques. The first technique involved compression molding a blend of PCL, glycerin, various amounts of HA powder, and a water extractable material of various particle sizes. Following the compression molding, the particles were extracted with de-ionized water yielding scaffolds of various pore sizes. The second technique involved electrospinning. A PCL/HA solution in acetone was formulated and electrospun onto an aluminum plate, resulting in a matrix of PCL fibers surrounded by beads of HA and PCL. The research goals are; characterization of the scaffolds with SEM and TEM prior to seeding of the cells; and examination of the extent of penetration and viability of the incubated cells using SEM. TEM will be utilized in characterizing the electrospinning samples, examining fiber size, shape and networking. SEM will gather information on pore size, distribution, and shape (CM samples), information on fiber size and shape and the presence of ceramic deposits (ES samples) as well as determining the extent of cell penetration into the scaffolding. The sample(s) that are most viable for cell growth will be determined once all of the analysis has been completed.

C11.30
PATTERNING CELLS USING THE H-BONDED POLY-ELECTROLYTE MULTILAYER TEMPLATE. Sung Yun Yang, Michael F. Rubner, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

Ultra thin polymer films that were prepared via layer-by-layer deposition of polyacrylamide and weak polyelectrolytes showed a great resistance to mammalian cell-attachment. Hydrogen bonding within the multilayers is stable at low pH but disrupted at high pH. This property enabled micropatterning of the multilayers by a selective stabilization process, crosslinking by heating or UV-irradiation, using ink-jet printing or photolithography. Patterns created by these subtractive patterning methods were used for controlling the growth of mammalian cells. In order to understand the cell resistance of the films, protein binding onto the multilayer was studied by surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) techniques. This type of patterning technique has a great potential in biosensors and tissue engineering.

C11.31
DNA DIRECTED MAGNETIC NETWORK FORMATIONS WITH FERROMAGNETIC NANOPARTICLES. H.Y. Lee, Y. Sacho, T. Kanki, I. Terawaki, H. Tanaka, and T. Kawai, The Institute of Scientific and Industrial Research, Osaka University, Osaka, JAPAN; J.W. Cheon, J.H. Yoon, Department of Chemistry, Yonsei University, Seoul, KOREA.

Deoxyribonucleic acid (DNA) is the fundamental material in life sciences. Recently, the DNA template method has attracted attention for nanostructure construction. Also, particle assembly of functional materials at the nanometer scale is an important objective of nanotechnology which can provide innovative materials and devices. For example, for magnetic recording media, ferromagnetic nanoparticle systems isolated by nanometer scale distance are an important technique to realize Magnetic Random Access Memory (MRAM) which takes advantage of spin tunneling magnetoresistance (TMR) phenomena. We formed a DNA network embedding ferromagnetic cobalt nanoparticles with 12 nm diameter through nano-scale self-assembly of DNA molecules and confirmed its structural characteristics using an atomic force microscope. Moreover, non-contact magnetic force microscope (MFM) measurement revealed that some embedded cobalt nanoparticles have different directions of magnetization, similar to "bits" in magnetic data storage devices. We will present formation of a DNA network structure embedding ferromagnetic cobalt nanoparticles through nano-scale self-assembly of DNA molecules; it also reports their structural and magnetic characterization by scanning probe microscope (SPM).

C11.32
CONTROLLED TAILORING OF DNA CHAIN LENGTH THROUGH DNA/LDH NANOHYBRID SYSTEM. Jae-Min Oh[a], Seo-Young Kwak[b], Jin-Ho Choy[a]; [a]Seoul National University, Seoul, KOREA; [b]University of Illinois, Urbana, IL.

The length of DNA double helix was successfully manipulated by DNA/LDH nanohybrids. DNA was intercalated into layered double hydroxide (LDH), $Mg_2Al(OH)_6(NO_3)$ $0.1H_2O$, through ion exchange method. Since the LDH diameter ($\approx$ 200 nm) is smaller than the chain length of DNA, some parts of the intercalated DNA chains are exposed outside of the host LDH layer. The exposed parts could be trimmed by enzymatic or chemical treatment, which led to relatively precise control of DNA chain length according to the size of host LDH. And the recovery of DNA with controlled length can be achieved by treating the DNA/LDH hybrid in an acidic solution, which was confirmed by the electrophoresis analysis. The size of recovered DNA molecule was determined to be about 500 bp long ($\approx$ 170 nm), which is fairly well consistent with the average size of LDH ($\approx$ 200 nm). Since the sizes of LDHs are easily controlled from 50 to 350 nm within narrow size distribution by various synthetic methods, the chain length of DNA molecule can also be manipulated by the size of the host LDH. This study implies that easily prepared and controlled inorganic materials can be potential candidates for bio-molecule manipulating agents.

C11.33
NANOSTRUCTURED BIOCOMPOSITE AEROGELS. J.M. Wallace, J.W. Long, J.K. Rice, R.M. Stroud, and D.R. Rolison, Naval Research Laboratory, Washington, DC.

Composite aerogels, highly porous, high-surface-area materials, can be formed by "nanogluing" the appropriate guests into the network of an about-to-gel silica sol. The resultant composite gel retains the bulk and surface properties of the silica framework and adds those of the incorporated guest, which can range in size over six orders of magnitude. Recent results indicate that biocompatibility can also be engineered into the silica aerogel nanoarchitecture. We have nanoglued heme-containing proteins into the silica network during sol-gel processing with drying from hexane to produce protein-composite silica ambigels; these directly nanoglued proteins do not remain viable under aerogel processing conditions, however. We have recently demonstrated that colloidal gold can structure and stabilize heme proteins such that these gold-protein composites can be supercritically dried to produce biomimetic supramolecular architectures. Structural and conformational changes, as well as molecular accessibility, were optically detected once the protein was incorporated into the gel matrix. The composite aerogel can then be used to sense in real time such gas- and liquid-phase heme-binding analytes as CO and NO. The sensing response is so rapid because the silica matrix provides a continuous three-dimensional architecture with a continuous pore network for enhanced molecular transport.

C11.34
"STICKY" POLYMERS: ACTIVATED POLY(PHENYLENE ETHYNYLENE)S FOR BIOCONJUGATION AND SURFACE FUNCTIONALIZATION. Jordan H. Wosnick, Timothy M. Swager, Massachusetts Inst of Technology, Dept of Chemistry, Cambridge, MA.

Poly(phenylene ethynylene)s (PPEs) are a class of conjugated polymers that are of major interest both in theoretical investigations and for the construction of highly sensitive chemical sensors based on the "molecular wire" effect. Previous uses of PPEs in sensory schemes have relied on the incorporation of receptor units directly into the polymer backbone. Using specially designed "sticky" monomers bearing amine-reactive side-chains, we have been able to effect post-polymerization modification of PPEs with molecules of biological interest both in solution and in film form. We have also applied this methodology toward the attachment of PPEs to surfaces. The resulting modified PPEs have been used for sensing biomolecules and in assay schemes. This methodology is modular and allows for the construction of a range of different sensory devices.

C11.35
A MODEL BIOSENSOR USING THE AVIDIN-BIOTIN SYSTEM AND SELF-AMPLIFYING CONJUGATED POLYMERS. Juan Zheng, Timothy M. Swager, Massachusetts Institute of Technology, Dept of Chemistry, Cambridge, MA.

We have constructed a model biosensor based on poly(phenylene ethynylene)s (PPEs) and the tight binding interactions of the biotin-avidin system. Conjugated polymers such as PPEs lend themselves to a variety of methods for signal transduction in a sensing event, as changes in optical properties can occur as a function of pH, oxidation state and conformation. We are investigating interchain interactions as a sensitive and highly specific method for analyte detection, taking advantage of the multivalent nature of the interaction of avidin with biotin to aggregate the biotinylated polymer chains. A variety of biotinylated polymers were synthesized with differing linker lengths and their interactions with avidin were found to produce a transducible sensory response.

C11.36
NOVEL PROPERTIES OF CARBON NANOTUBES FUNCTIONALIZED BY METAL COMPLEXES. Andrew Minett, Sakina Benrezzak, Manuel Ruether, Dept. of Physics, Trinity College Dublin, Dublin, IRELAND; Fiona Frehill, Johannes Vos, National Centre for Sensor Research, Dublin City University, Dublin, IRELAND; Marc in het Panhuis, Functional Materials Group, Dept. of Physcis, Trinity College Dublin, Dublin, IRELAND.

The chemical modification of nanoscale materials has created increasing interest in novel hybrids for application in molecular devices. For the reaction of amino- functionalised multi-walled carbon nanotubes with a redox active inorganic complex we have observed an unexpected number of both Y- and T-junctions within a nanotube thin film. The development of nanoscale electronics can benefit from such features through the generation of superior heterojunctions and interconnects. Results of preliminary emission data obtained in solution suggest that this material also has the potential for either electrical or optical-based sensing. Characterisation techniques such as atomic force and transmission electron microscopies, NMR, and UV-vis spectroscopy have been employed to determine the novel properties resulting from the nanotube-complex reaction.

C11.37
STRUCTURE AND PROPERTIES OF POLY(α-HYDROXYL ACIDS)/NANO HYDROXYAPATITE COMPOSITE SCAFFOLDS. Guobao Wei, Peter X. Ma, Univerisity of Michigan, Department of Biomedical Engineering, Department of Biological and Materials Science, Ann Arbor, MI.

Tissue losses and organ failures resulting from injuries or diseases

remain frequent and serious health problems despite great advances in medical technologies. Transplantation and reconstructive surgeries are seriously challenged by donor tissue shortage. We take a tissue engineering approach to design 3D scaffolds for cells to grow and synthesize new tissues. The scaffolds are biodegradable and will resorb after fulfill the purpose as 3D templates, leaving nothing foreign in the body. To better mimic natural bone structurally, mechanically and biologically, nano-sized hydroxyapatite particles (N-HAP, mimicking bone mineral) are formulated with biodegradable poly(α-hydroxyl acids) to form composite scaffolds with well-controlled pore structures using thermally induced phase separation (TIPS) in this work. The pore structure and mechanical properties of the scaffolds were optimized by the use of multiple solvent systems, different quenching rate and quenching depth. Fabricated scaffolds have porosities higher than 90% and average pore sizes ranging from 50 to 500 μm. The scaffolds containing N-HAP maintained open and regular 3D pore structure similar to those of pure polymer scaffolds, implying that N-HAP particles were dispersed within the polymer pore walls of the scaffolds. The addition of N-HAP increased the compressive modulus by 20$\sim$80% over that of pure polymer scaffolds. These results indicate that poly(α-hydroxyl acids)/N-HAP scaffolds may provide excellent 3D substrates for bone tissue engineering.

C11.38
CONTROLLED FUNCTIONALIZATION OF VARIOUS SUBSTRATES WITH DNA. Baocheng Yang, Sejong Kim, Shifeng Hou and Fotios Papadimitrakopoulos, Univ. of Connecticut, IMS, Department of Chemistry, Storrs, CT.

The organization of nano-sized & micro-sized assembled materials with the help of DNA has drawn more and more attention recently. It is due to the unique molecular recognition of DNA Synthons and temperature dependence of its hybridization process. To achieve its fully potential for hierarchic assembly, the proper molecular orientation of DNA for complex surfaces, suitable hydrophobic/hydrophilic interaction between DNA and surfaces, and the removal of non-specific binding of DNA on surfaces are needed to be obtained. Hereby, we utilized a modified coupling method by adding a capping step before the final conjugation of DNA with substrates to successfully prevent the non-specific binding of DNA on substrate surface and attain the desired non-collapsed conformation of DNA. Various substrates from glass, quartz to silicon are used in this study and showed the similar results. Different spectrometric methods such as UV-Vis, Contact Angle, Ellipsometry and XPS, are used to characterize the DNA functionalized substrates. Finally, the limitation of this method to some particles is addressed and the alternative method for water-stable particles is proposed and studied.

C11.39
WELL-DEFINED ORGANIC/INORGANIC HYBRID NANOPARTICLES BY ATOM TRANSFER RADICAL POLYMERIZATION. Thomas A.P. Seery, Dongqi Qin and Mark Jordi, Institute of Material Science and Chemistry Department, University of Connecticut, Storrs, CT.

Well-defined nano-scale polymer coated silica particle hybrid materials were prepared by using atom transfer radical polymerization (ATRP) to graft polymer chains "from" the particle surfaces. The procedure utilizes ultra small silica nanoparticles (D= 27.2 nm) with tethered ATRP initiators for "growing" well-defined vinyl polymers from the particle surfaces. The syntheses of polystyrene/silica and poly(t-butyl acrylate)/silica nanocomposites were carried out in a homogeneous DMF reaction mixture. The products were characterized by FT-IR, proton NMR, elemental analysis, TEM, thermogravimetry, and dynamic light scattering of both hybrid particles and the original initiator coated particles. The molecular weight and molecular weight distributions of the grafted polymers can be obtained using GPC after etching the silica cores with HF and we have done this with aggregated particles. The results show that the polymers attached on the silica particles were well-controlled with low polydispersity. It is demonstrated that well-defined polymer chains were grown from tethered initiators on silica surfaces to produce hybrid materials comprising a silica core and a well-controlled outer PSt or PtBA layer. PtBA polymers can be deprotected to form water soluble acrylic acid this procedure is expected to provide water soluble hybrid materials.

C11.40
ICOSAHEDRAL VIRUS ASSEMBLIES FOR USE AS PHOTONIC CRYSTALS. S.B. Juhl, R.A. Vaia, Air Force Research Laboratories, Wright Patterson Air Force Base, OH; Y. Ha, E. Thomas, Massachusetts Institute of Technology, Dept of Material Science and Engineering, Cambridge, MA; V. Ward, University of Otago, Dept of Microbiology, Otago, NEW ZEALAND.

Photonic crystals facilitate the coherent localization of electromagnetic waves due to the forbidden frequency bands created by the periodic nature of the materials index of refraction, which make them essential to Air Force applications ranging from sensors to communication. Some challenges to organic-based photonic crystal fabrication include reproducible creation of large-scale uniform structures with controlled periodicities of 100-400 nm, intricate methods of fabrication, and packing restrictions associated with spherical building-blocks. Biology has many opportunities for the advancement of photonic materials due to the large number of naturally occurring self-assembled photonic crystals. Using a bottom-up methodology, where smaller species are arranged together to form 1D, 2D, and 3D structures, virus particles are investigated as building blocks for photonic assembles. Virus particles are comprised of a precisely-defined protein assembly which creates monodisperse geometric shapes ranging in size from 30-300 nm. The spatially specific surface functionality arising from the proteins and unique geometries open novel approaches to manipulation and non-fcc packing. This work will explore various methods of assembly including capillary flow, electrophoresis, surface chemistry, and physical patterning through the use of high-thru-put concepts to assemble icosahedral virus capsids of the cowpea mosaic virus (comovirus) and iridovirus (iridoviridae). Morphological and optical characteristics of the assemblies will be discussed.

C11.41
DNA TEMPLATING OF ETHYLENE OXIDE COATED NANOCLUSTERS. S. Jhaveri, E.E. Foos, M.G. Ancona, A.W. Snow, M.E. Twigg, E. Chang, E. Goldman, Naval Research Laboratory, Washington, DC; L. Pilobello, D. Lowy, Nova Research, Alexandria, VA.

Progress in science and technology at nanometer scales is primarily limited by the difficulties of fabrication. One promising strategy is to harness some of natures nanofabrication machinery to develop novel techniques for the design, organization and assembly of nanoscale systems. We report here on a "codon-like" approach that utilizes DNA templating to organize gold nanoclusters. We employ ethylene-oxide-coated clusters that, unlike those used in other similar work, are a direct water-soluble analog of the common alkanethiol gold clusters in which tri- or tetra-ethylene oxide is used in place of the alkanethiol. These clusters are charge-neutral and quite stable and are capable of undergoing thiol substitution reactions. By attaching different ssDNA oligos to these clusters and isolating the products using gel electrophoresis we have created "nanocluster codons". Subsequent hybridization of these conjugated clusters to complementary ssDNA templates will demonstrate an assembly technique in which DNA code is translated into a cluster sequence in almost direct analogy with the biological process wherein DNA is translated into an amino acid sequence.

C11.42
DEVELOPMENT OF SMALL PEPTIDES FOR BINDING OF CARBON NANOTUBES. R.H. Smith, L. Lopatiuk, B.A. Little, D.A. Walters, Univ of Central Florida, Dept of Physics, Orlando, FL.

Peptides that bind to single-wall carbon nanotubes (SWNTs) have been found via phage display and biopanning. Our biopanning began with a library of bacteriophage M13 displaying random peptides as a fusion with the PIII coat protein. This library was incubated in buffer on immobilized carbon nanotubes produced by pulsed laser vaporization or high pressure CO (HiPco) methods. Bound phage were eluted in a low pH buffer to disrupt binding interactions and this raw eluate was amplified in E. Coli. The amplified eluate was further enriched in binding peptides by repeated panning under more stringent conditions. After multiple rounds of panning, the raw eluate was plated at high dilution so that individual phage clones with unique peptide sequences could be isolated. Clones were sequenced and assayed for binding to inorganic substrates (including carbon nanotubes, graphite, and mica) via several methods. Atomic force microscopy revealed that two of the phage clones isplayed binding to SWNTs with different affinities. The amino-acid sequences of the displayed peptides differ greatly, suggesting distinct structures and/or binding mechanisms.

C11.43
ASSESSMENT OF CHEMICAL AND PHYSICAL PROPERTIES OF PROTEINS IN SOL-GEL GLASSES. Lymari Fuentes, Jessica Oyola, Reginald Morales, Edwin Quinones, University of Puerto Rico, Department of Chemistry, San Juan, PR.

The interest in immobilizing proteins in porous materials stems from the possibility of enhancing their chemical and thermal stability, to catalyze reactions under non-physiological conditions and to develop sensing devices. We report on experiments carried out on phospholipase (PLA) and azurin immobilized in a sol-gel glass. It was found that PLA is active in the sol-gel glass, monitoring the hydrolysis reaction of an artificial phospholopid. The kinetics of the model reaction was studied as a function of calcium, which is the co-factor. The chemical stability of azurin was assessed using

guanidine hydrochloride as a denaturing agent. The gradual denaturation of azurin upon adding guanidine was detected monitoring the red shift in the fluorescence band of tryptophan. Using acrylamide as a quencher, it was possible to monitor the transport of this quencher through the interstices of the matrix as well as probe the accessibility of the tryptophans of the entrapped proteins. These experiments show marked difference between the behavior of the enzyme entrapped in the sol-gel and the enzyme free in solution.

C11.44
SELF-ASSEMBLY OF THE GLASS-CERAMICS/CdSe/ENZYME AGGREGATIONS IN THE OPTICAL TRAP. Andrey Zavalin, W. Eugene Collins, Steven Morgan, Dept of Physics, Fisk Univ, Nashville, TN.

The main advantage of the one-beam optical trap configuration is simplicity and a wide spectrum of applications. The quasi-micron size of the optical trap zone and the possibility to control position and motion precisely can satisfy the requirements of micro-manufacturing in integrated optics and optical sensors, photonic crystals and bio-chip production. In our previous experiments [1] for behavior of many particles, trapped in the gradient one-beam optical trap it has been shown that trapped particles create quasi-molecular dynamic structures, assembled together by photons and existing only in presence of laser field. Under the certain conditions photon bonding is converted to the chemical bonding. In the present work the aggregations, created in 2-component solution are studied. The particles of porous glass-ceramic of CaO-TiO2-P2O5 system and 1-50 um size were mixed with CdSe/TOPO 20 nm particles in toluene. Dynamic aggregations up to 300 um size were created inside the optical trap. These aggregations were compared with one-component glass-ceramic or CdSe aggregations created in different solvents. In additional experiments different enzyme molecules were also studied as bonding agents for glass-ceramic particles. Micro-Raman spectra have been taken from dynamic and stable permanent aggregations in solution and in dry condition. Obtained spectra show several new peaks which could be associated with creation of new chemical bonds. Micro-Raman spectra are presented and possible mechanisms of bonding are discussed. 1. W. Eugene Collins, Weijie Lu, Steven Morgan, and Andrey Zavalin, C60 Clusters Self-Assembly in One-beam Optical Trap, MRS Symp. Proc. Vol. 675, p. W1.6.1-W1.6.4.

C11.45
SELF-ASSEMBLY AND POLYMERIZATION OF BIOMIMETIC COLLOIDS USING PEPTIDE-AMPHIPHILES. Raymond Tu, University of California-Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; Markus Biesalski, University of Freiburg, Institute for Microsystem Technology, Freiburg, GERMANY; Matthew Tirrell, University of California-Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA.

Biological systems depend on the ability to specifically assemble molecules in a complex environment that includes a variety of components and membrane bound compartments. Peptide-amphiphiles were developed to access and control this machinery with a synthetic molecule that combines a peptide head-group covalently linked to a hydrocarbon tail. This work looks into a polymerizable amphiphilic architecture, where the design contains a monomeric element, amphiphilic character, and biospecific peptide structure (coiled-coil helix associated with the GCN4 sequence known to bind regions of DNA). The polymerization of the peptide amphiphile occurs in an emulsion polymerization format, where the peptide amphiphile serves two roles. First, it acts as a sufactant and participates in micelles that nucleate the formation of polymeric colloids. Second, the amphiphile is a co-monomer that polymerizes with the methylmethacrylate or styrene monomer. Co-surfactants, namely, SDS, triton X-100 and polysorbates are included to template the formation of micelles and, simultaneously, functionalize the interface of the colloid. Circular dichroism results show that the peptide amphiphile has a stable alpha-helical secondary structure, which is a pre-requisite for bio-mimetic function. Gel permeation chromatography coupled with dynamic light scattering confirms the formation of polymers, yielding colloids that are 20-50 nm in diameter. This type of molecular construction has allowed us to prepare a peptide-functionalized co-polymer using a "bottom-up" approach. These assemblies of polymerized peptide-amphiphiles allow for the rational design of biomimetics that can specifically interact with a variety of ligands, and this ability to decorate the interface with covalently linked peptides will be useful as a platform to probe DNA-peptide binding.

C11.46
ORDERED POROUS TEMPLATES AND REPLICAS IN BIOTECHNOLOGY. Ulrike Rehn, Petra Göring, Kornelius Nielsch, Sven Matthias, Ralf B. Wehrspohn, and Ulrich Gösele, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

Porous membranes are used in several areas of biotechnology. We have developed over the last 5 years processes that allows us to prepare highly ordered pore arrays with pore sizes in the range of 25 nm to few microns. These pore arrays consists of either silicon or alumina. The inner walls of the pores can be further functionalised by noble metals or biocompatible polymers [1]. Moreover, these structures can also be replicated creating very monodisperse metal nano- or μ-wires (Ag, Au, Ni, Co, Cu). We will discuss the applicability of the porous materials in two areas: the use as analytical systems and as biomarkers. Lipid bilayers are used to study drug pathways through cells. For example, we study together with our project partners the drug transport through epithelial cells which are cultivated on top of the porous templates [2, 3]. On the other side, biological molecules could also be used in a more technological way. Using different replicated metal wires or prepare different surface design, the wires can be used as biomarkers [3]. For example, if the porous template is three dimensionally structured, so are the metal μ-wires. This yields a strong contrast in the reflectivity which can be detected with an optical microscope. DNA and proteins could be linked to these μ-wires. [1] M. Steinhart et al., Science 296, 1997 (2002). [2] Hennesthal, C. and Steinem, C. J. Am. Chem. Soc. 122, 8085 (2000). [3] Nanobiotechnology project NBT064, German Ministry of Science and Research. [4] Nicewarner-Pe ña et al. Science 294, 137 (2001).

C11.47
INVESTIGATION OF SUPPORTED LIPID BILAYERS ON A NANOPOROUS THIN POLYMER FILM. Steven Kolthammer and Shenda M. Baker, Department of Chemistry, Harvey Mudd College, Claremont, CA.

Pore-spanning lipid bilayers provide a model system that demonstrates greater stability than freely suspended memgranes without hindering the lateral mobility of membrane components. Such systems allow for the incorporation of functional transmembrane proteins and are therefore of interest to fundamental biophysical research as well as for the construction of novel biosensors. Ordered nanoporous templates have been created from the cylindrical morphology of poly(styrene)-b-poly(methyl methacrylate) (PS-PMMA) on silicon substrates. UV exposure followed by rinsing with appropriate solvents removes the PMMA and produces a cross-linked PS film (approximately 30nm thick) with hexagonally ordered pores, diameters from 10 to 40 nm depending on the molecular weight of the copolymer. From this ordered template, etched silicon and gold-coated substrates were fabricated. Langmuir-Blodgett and other techniques were used to form single bilayers as well as alighned lipid multilayers on both flat and porous substrates. Neutron reflectometry, elipsometry, contact angle measurements and atomic force microscopy were utiliezed to investigate the resulting structures.

C11.48
PRODUCTION OF CoPt ALLOY GRAINS WITHIN PROTEIN TEMPLATES. B. Warne, D. Gleeson, R. Jones, A. Nartowski and E. Mayes, NanoMagnetics Ltd., Bristol, UNITED KINGDOM.

Nanoparticles of equiatomically alloyed $L1_0$ phase CoPt have been considered for ultrahigh density magnetic recording as well as permanent magnet applications. Aqueous synthesis has demonstrated outstanding size control in the preparation of CoPt nanoparticles, but the production of monodisperse precursors for the $L1_0$ phase of CoPt has only been demonstrated using the protein ferritin. The spherical protein ferritin can be used as a generic reaction vessel for the production of a variety of materials, such as iron and manganese oxides. It has also been used for the production of superparamagnetic magnetite and semiconducting cadmium sulphide. In all instances the protein was used not only to encapsulate, but to tightly regulate the size of the nanoparticles formed. This monodisperse protein strictly regulates the maximum diameter of nanocrystals synthesized within its 8 nm diameter cavity. We report on recent progress using the ferritin protein as a template for CoPt alloy nanoparticles and propose various mechanisms for nanoparticle formation within protein templates. Electromicrographs and crystallographic data are presented to confirm the formation of equiatomic CoPt alloy within the protein.

C11.49
HIGH GRADIENT SEPARATION OF MONODISPERSE MAGNETIC NANOPARTICLES. A. Bewick, J. Hoinville, O. Kasyutich, B. Warne, and E. Mayes, NanoMagnetics Ltd., Bristol, UNITED KINGDOM.

We report on the challenges in the selective separation of magnetic nanoparticles from a suspension. The suspension contains a range of particle sizes and particle moments, and the aim of the separation process is to narrow the size and moment distributions of the nanoparticles within the suspension. High Gradient Magnetic Separation (HGMS) systems are commonly used to fractionate suspensions of cells decorated with multiple magnetic particles giving

each cell a relatively high magnetic moment. We have used HGMS to fractionate suspensions containing nanoparticles of magnetite and CoPt prepared within a protein template. The nanoparticles have a relatively low magnetic moment, but both continuous flow and wire capture systems have demonstrated promising results. The particle size and moment distributions of the source material are compared with those of the separated material by TEM and temperature dependent SQUID magnetometry.

C11.50
DNA-ASSISTED 2D PHOTONIC CRYSTAL FABRICATION.
Fotios Papadimitrakopoulos, Sejong Kim, Baocheng Yang, and Shifeng Hou, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT.

DNA-oligomers and their hybridization have attracted much interest among chemists and material scientists as part of their distinctive ability to recognize its complementary sequence and melt according to its length and composition dependent sequence. In this paper, we utilize for the first time these DNA properties for the fabrication and immobilization of 2-dimensional photonic crystals of monodispersed colloidal microspheres. Utilizing a variety of surface grafting techniques, amine-terminated DNA oligomers were covalently attached to both polystyrene colloidal particles and silicon substrates. Following the capillary-induced organization of DNA-decorated microspheres into close-packed 2-D opaline arrays, the first monolayer was immobilized using the non-covalent hybridization while unwanted multilayers were successfully removed. Various salt/buffer systems were investigated to optimize colloidal stability, its ability to self-organized into large 2-D crystalline domains as well as increase DNA-hybridization strength. Analytical techniques, such as XPS, spectroscopic ellipsometry, UV-spectroscopy, sessile-drop contact angle and scanning electron microscopy, have been performed for characterization at all stages. This technique is presently investigated for the layer-by-layer assembly of 3-D opaline arrays, where controlled insertion of defects is assisted via surface-selective DNA hybridization.

C11.51
MOLECULAR SIMULATION OF BIO-INSPIRED PROGRAMMED ASSEMBLY OF NANOSCALE BUILDING BLOCKS. L. Booth, T. Chen, M. Horsch, M. Lamm and S.C. Glotzer, Dept. of Chemical Engineering, University of Michigan, Ann Arbor, MI.

Pioneering experiments by several groups have demonstrated that DNA and other biomolecular or synthetically-programmable polymers can be used as assemblers of one-, two- and three-dimensional nanoparticle arrays in solution and on surfaces. Control over the structures that form by tuning conditions such as temperature and nanoparticle size has been demonstrated, suggesting that it may be possible to use these bio-inspired approaches for large-scale fabrication of functional nanostructures. Inspired by these works, we are developing simulation strategies for modeling DNA-mediated and polymer-mediated assembly of nanoscale building blocks, such as quantum dots, nano-colloids, nanorods, and silica cubes, to help interpret experiments and suggest viable assembly methodologies. In this talk, we present preliminary results of molecular dynamics, Brownian dynamics, and Monte Carlo simulations developed to elucidate fundamental principles of ordering processes in these systems over a range of length and time scales.

C11.52
ANALYSIS OF SUBCELLULAR MECHANICAL ACTIVITY IN ENGINEERED CARDIAC TISSUE ON ELASTIC SCAFFOLDS.
E. Guan, State Univ of New York at Stony Brook, Dept of Materials and Engineering, Stony Brook, NY; Emilia Entcheva, Harold Bien, State Univ of New York at Stony Brook, Dept of Biomedical Engineering; Miriam Rafailovich, Jonathan Sokolov, State Univ of New York at Stony Brook, Dept of Materials and Engineering, Stony Brook, NY.

We developed and tested a novel image processing technique for subcellular analysis of contractile activity in engineered cardiac tissue constructs. The essence of the proposed technique is the application of digital image correlation (DIC) to time series of video images of spontaneous or electrically-triggered contractile activity. Naturally occurring microscopic inhomogeneities on the cell surface served as features, facilitating the motion tracking. The average deformation in term of displacement around any point in the digital images was calculated by a normalized cross-correlation function. The sub-image used to calculate average displacement is 51*51 pixels in size for these tests. The spatio-temporal resolution of our algorithm was determined by the recording video equipment. For this study, the time resolution was 30Hz; the spatial resolution, which is corresponding to the size of sub-image size, was 50mm and displacement accuracy was about 0.1mm. Neonatal rat ventricular cells were isolated and cultured to form syncytium on flat rigid (polyvinylchloride), F, or elastic topographically modified scaffolds (polydimethylsiloxane), EM, coated with fibronectin. The EM-grown cell networks developed synchronized contractile activity. Video sequences were recorded from the cell constructs on day 5-6 after culturing using a digital video camera attached to an inverted microscope. Vector and component maps of displacement were obtained with the DIC algorithm. Our results revealed complex heterogeneous displacements in the F-grown cell structures. The EM-grown cells exhibited anti-phase displacements across grooves on the scaffold surface. The DIC technique could become a valuable tool in functional characterization of tissue engineered muscle constructs.

C11.53
ASSEMBLY OF ASYMMETRIC BILAYERS AND FORMATION OF HYBRID VESICLES. Sophie Pautot, D.A. Weitz, Harvard University, Dept of Physics and DEAS, Cambridge, MA; Barbara J. Frisken, Simon Fraser University, Dept of Physics, Burnaby, BC, CANADA.

The chemical and mechanical properties of the cellular bilayer depend on the lipid composition and, in particular, on the asymmetric distribution of these molecules within the bilayer. Up to now, the techniques available for preparing vesicles with asymmetric bilayers have been limited because vesicle preparation techniques were based on the spontaneous assembly of lipid molecules into bilayers, which leads to an even distribution of the lipid molecules on the inner and outer leaflets of the bilayer. Obtaining vesicles with partially asymmetric lipid bilayers has required the use of chemicals or other methods to perturb the distribution. Here we describe the systematic engineering of unilamellar asymmetric vesicles based on the assembly of two independently-prepared monolayers. We show that the desired composition can be set regardless of the charge or spontaneous radius of curvature of the molecules and that, in the absence of stimulation, the distribution remains constant for at least twenty-four hours. Finally, we demonstrate the generality of the process by constructing hybrid bilayers composed of both polymer and surfactant molecules, where the polymer provides mechanical support for the bilayer, while the lipids provide biocompatibility.

C11.54
FABRICATION OF STIMULUS-RESPONSIVE POLYMERIC NANOSTRUCTURES BY PROXIMAL PROBES. Sang-Jung Ahn, Jinho Hyun, Woo Lee, Ashutosh Chilkoti, and Stefan Zauscher; Department of Mechanical Engineering and Materials Science and Department of Biomedical Engineering, Duke University, Durham, NC.

The triggered control of interfacial properties on the nanometer scale holds significant promise for actuation in bio-nanotechnology applications, where polymeric actuators may manipulate the transport, separation, and detection of many biomolecules. To fabricate stimulus-responsive polymer brushes we have developed several complementary methods that combine surface initiated polymerization (SIP), reactive "dip-pen" nanolithography (DPN), and scanning probe annodization lithography. Our in-situ coupling and polymerization reactions use commercially available reagents to minimize the labor involved in synthesis and purification. To illustrate our method, we present the amplification of a DPN patterned self-assembled monolayer (SAM) by SIP of N-isopropylacrylamide (NIPAAm). The patterned substrates are fabricated by DPN of 16-mercaptohexadecanoic acid on ultra-flat, template stripped gold, immobilization of an initiator, and subsequent polymerization of NIPPAm. It appears as if the thickness of the polymer brush layer that can be achieved is a function of the lateral feature size. Lateral scales on the order of micrometers yield layer thicknesses of about 5 nanometers, corresponding to about 50 monomer units. As the lateral scale decreases to tens of nanometers, the thickness of the polymer brush layer decreases to monomolecular sizes. While in an aqueous environment the change of polymer thickness took place reversibly at the critical solution temperature, no changes in brush conformation were observed in an organic solvent.