SYMPOSIUM AA
Dynamic, Self-Organizing Systems in Multifunctional Nanomaterials and Nanostructures
March 28 - April 1, 2005

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* Invited paper
SESSION AA1/S1: Joint Session: Self-Assembly of Magnetic Nanoparticles
Chairs: Dhannanjay Kumar and Ralph Nuzzo
Tuesday Morning, March 29, 2005
Room 3005 (Moscone West)

8:40 AM *AA1.1/S1.1

Colloidal nanocrystals with controlled crystal shape, structure and surface passivation are now increasingly available. This talk will focus on the interesting superlattice systems that can be built with two types of these "artificial atoms". We combine a high temperature solution phase synthesis with size selective processing techniques to produce organically passivated magnetic and semiconducting nanocrystals with size distributions less than 5%. Procedures have been developed for Co, Ni, FePt, CoPt3, Fe3O4 and Fe2O3 magnetic nanocrystals as well as for CdSe, PbS, PbSe and PbTe and semiconductor quantum dots. Examples of binary superlattices with AB13, AB2 and AB5 structures will be discussed along with other potential structure incorporating 2 distinct types of nanocrystals as the building blocks.

8:50 AM *AA1.2/S1.2
Arrays of Magnetic Nanowires via Block Copolymer Templates. Thomas P. Russell and M. Tomislav Mijakovic. Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; 2Physics Department, University of Massachusetts, Amherst, Massachusetts.

Arrays of magnetic nanowires and nanowire devices were fabricated using nanoporous templates derived from self-assembling diblock copolymer films. Poly(styrene-methacrylate) (PS-PMMA) diblock copolymers as porous templates that were used to fabricate hexagonal arrays of vertical nanowires with densities of exceeding 150,000 per square inch. Electrodeposition within the template produces 10-mm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanence making them potential candidates for ultrahigh-density perpendicular magnetic storage media. The internal crystal morphology of the nanowires, and consequently magnetic properties, can be manipulated and tuned by electrodeposition process parameters. The copolymer templates have been patterned laterally using conventional lithographic exposure to fabricate novel 3D magnetic nanowire devices. This includes current-in-plane magnetoresistive devices and current-through-wire switching field devices. Anisotropic magnetoresistance measurements show a sharp and complete magnetization reversal, indicating single-domain nanowire switching behavior. Such properties offer promising potential for new magnetic nanodevices built upon this new domain-state switching behavior. This work is supported by National Science Foundation Nanoscale Interdisciplinary Research Team, Materials Research Science and Engineering Center and the Department of Energy.
Recent studies on Co and permalloy rings have shown that a totally flux-closed magnetic vortex state could be stable at remanence. The two characteristics of this vortex, clockwise and counterclockwise, have been proposed as the carriers for the stored information. Our in-field magnetic imaging demonstrated that on subsequent field cycles the chirality of the large portion of individual rings was fixed. Earlier, we suggested that the shape effects are responsible for the vortex formation and chirality in circular elements. Furthermore, using micromagnetic modeling, we have ascertained that small asymmetry in the shape of ring is sufficient to produce preferential chirality. The modern micromachining techniques and self-organizing aggregates shape changes. The results show that with the knowledge of the asymmetry present, we can predict the switching direction accurately.

SESSION AA2: Building Blocks and Novel Structures I
Chair: Ralph Nuzzo
Tuesday Morning, March 29, 2005
Room 3011 (Moscone West)

10:30 AM   AA2.1
Controlled Synthesis of II-VI Semiconductor Nanostuctures Using Microemulsion and Liquid-Crystal Templates. Georgios N. Karanikolos, Nga-Leung Vera Law, Paschalis Alexandridis and T.J. (Lakis) Mountziaris, Department of Chemical and Biological Engineering, University of Buffalo, Buffalo, New York.

A scalable method for controlled synthesis of quantum dots and nanowires (nanorods) of II-VI compound semiconductors has been developed. The technique employs stable microemulsion and liquid-crystal templates, which are formed by self-assembly of a ternary system consisting of an amphiphile block copolymer, a polar continuous phase (formamide), and a non-polar dispersed phase (heptane) that forms spherical or cylindrical nanodomains. The controlled synthesis of bismuth telluride nanowires, ZnS quantum dots and single-crystalline nanorods has been demonstrated by reacting diethylzinc, dispersed in the heptane, with hydrogen selenide gas. Since diethylzinc is the limiting reactant, its initial concentration in the heptane was used to precisely control the size of the quantum dots or the diameter of the nanorods. The hydrogen selenide gas was either bubbled through the microemulsions or allowed to diffuse into the liquid-crystal templates to facilitate the synthesis of the nanoscale materials. ZnS nanowires formed by this method show an irreversible reaction between diethylzinc and hydrogen selenide. The nuclei grow by surface reactions and cluster-cluster coalescence to yield single-crystalline nanostructures having the shape of the confining nanodomains of the template. The localized energy release during these exothermic processes can explain the formation of the single-crystalline nanostructures in a medium that is at room temperature. The materials were characterized by photoluminescence and absorption spectroscopy, and by HRTEM. Techniques for extracting, passivating and functionalizing the quantum dots are under development to exploit their size-dependent luminescence in multiplexed optical microarrays and DNA microarrays. Promising results have been obtained from templated synthesis of CuCl and ZnSe synthesis in a different class of templates that employ water as liquid-crystal templates, which are formed by self-assembly of a mixture of cubes and tetrahedrons characterized by truncated corners and edges; monodisperse particle diameters ranging from 20 to 80 nm were obtained by limiting the reaction time. We propose that the defects inherent in twinned nuclei of silver led to their selective etching and dissolution by chloride and oxygen (from air) leaving only single crystal nuclei to grow. Through a simple galvanic replacement reaction, we have converted monodisperse 30 nm silver particles synthesized by this method into 40 nm gold nanocages. The high advantage of their extremely high extinction coefficients in the near-IR (800-1000 nm, transparent window for soft tissues), we subsequently functionalized gold nanocages with tumor antibodies to enable contrast-enhanced imaging of cancer tissue and photodynamic therapy of tumor cells.

11:00 AM   AA2.3

High yields of single crystal silver nanoparticles were synthesized for the first time in solution through the addition of chloride to a standard polycrystalline synthesis. The shapes of these nanoparticles were a macrocylic hexamers self-assemble to form large aggregate. The Preparation and Characterization of Mesostructured Thin Films of Perovskites and Ternary Oxides. Bernd Smarsly2, Benjamin J. Wiley, Jingyi Chen and Younan Xia; University of New Mexico, Albuquerque, New Mexico; 2Chemical & Nuclear Engineering Department, The University of New Mexico, Albuquerque, New Mexico; 2Department of Chemistry, University of Georgia, Athens, Georgia.

Considerable efforts have been devoted to nanostructured platinum because of its significance for environmental and technological consideration. It serves as a major catalyst for the reduction of tailpipe exhausts pollution to water and air. It is also the best catalyst for polymer electrolyte membrane (PEM) fuel cells. In addition, nanostructured platinum is of particular interest for sensors, bioensors and other devices, such as a high-frequency nanomechanical resonator based on platinum nanowires. All these applications of platinum are closely related to its size and shape. Hence, we describe a method of synthesis that leads to uniform, monodisperse, circular dendritic sheets and face-like platinum nanoshapes by chemical reduction of aqueous metal complex with ascorbic acid in the presence of liposome template. The nanoparticles were characterized with TEM, STEM, SEM, XRD, DTA-TGA, N2 adsorption and CV. Their formation mechanism was determined; moreover, synthetic control over the morphology of these nanofoams was realized using a tin-porphyrin photocatalyst to conveniently and effectively produce a large, high-particle population of catalytic growth centers, which resulted in uniform size of nanocages. These nanomaterials have potential applications, such as catalysis and sensors, due to their high surface area and self-assembled characteristics. This work was partly supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, and by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (DE-FG02-02ER15369). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

11:15 AM   AA2.4
Dendritic Platinum Nanostructures. Yufang Song1,2, Donovan Pena1, William A. Stemp1, Jennifer L. Piccir1, Darryl Y. Saeki1, Jamison E. Miller1 and John A. ShelnuttI;1;1Biomolecular Materials & Interfaces Department and Ceramic Process & Inorganic Materials Department, Sandia National Laboratories, Albuquerque, New Mexico; 2Chemical & Nuclear Engineering Department, The University of New Mexico, Albuquerque, New Mexico; 2Department of Chemistry, University of Georgia, Athens, Georgia.

The Preparation and Characterization of Mesostructured Thin Films of Perovskites and Ternary Oxides. Bernd Smarsly2, Benjamin J. Wiley, Jingyi Chen and Younan Xia; University of New Mexico, Albuquerque, New Mexico; 2Chemical & Nuclear Engineering Department, The University of New Mexico, Albuquerque, New Mexico; 2Department of Chemistry, University of Georgia, Athens, Georgia.

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Mesostructured thin films with a crystalline framework have attracted significant attention to their potential use in sensing and other applications. While oxides like TiO2 and CeO2 can now be obtained by using evaporation-induced self-assembly by a suitable novel block copolymer template ("KLE") [1], so far mesostructured perovskites and other complex oxides have not been available. Here we report for the first time the successful preparation of thin films of several perovskites (SrTiO3, Li2TiO3, LiTaO3) and ternary oxides such as Indium-Tin-Oxides (ITO) with mesostructural order [2]. These oxides possess interesting physical properties (dielectric SrTiO3, ferroelectric LiTaO3). Starting from metal chlorides or alkoxides, thin mesostructured films are dip-coated, the mesostructuring being established through a suitable type of block copolymer template. Afterwards, an appropriate temperature treatment is applied generating mesopores of ca. 10 nm and perovskite nanoparticles in the pore walls without disrupting and destroying the mesostructure. The polymer (KLE) was synthesized in our institute and has a hydrophilic PEO block and a poly(ethylene-co-butylene) hydrophobic block, showing advanced templating properties in terms of the thermal stability and hydrophilic-hydrophobic contrast [1]. Also, the block lengths were designed to be long enough to allow for sufficiently thick walls, i.e. nanocrystals in the pore walls of at least 5 nm, being compatible with the nuclei or in order to find an appropriate nucleation procedure, detailed in-situ combined Grazing Incidence Small-angle X-ray scattering (GIXS) and Wide-Angle X-ray Scattering (WAXS) studies were performed on these materials at the Synchrotron facility at Elettra (Trieste, Italy). By monitoring the crystallisation and mesostructure changes at the same time, the temperature could be adjusted to create films with perovskite nanoparticles in the mesopore walls whilst maintaining the mesostructural order, which was confirmed by High-Resolution Transmission Electron Microscopy (HRTEM) [2]. The present strategy to obtain mesostructural multi-shell oxide nanocrystalline films creates for the first time the bridge between conventional mesoporous materials and the remarkable properties of crystalline ternary or quaternary metallic oxides that highly contribute to the richness of solid state chemistry and physics. Initial syntheses of SrTiO3, La2TiO4, and LiTaO3 with varying size and shape of the nanocrystals were performed. Here, we report the ordered spherical and cylindrical morphologies of SrTiO3 nanocrystals by spin coating a blend of an amphiphilic triblock copolymer poly(ethylene oxide)132-poly(propylene oxide)50-poly(ethylene oxide)132 and poly(4-vinyl phenol) (MW=20,000) with a PEO side chain on a silicon wafer. The polymer blend microphase separates upon drying and the acid catalyst partitions selectively into the continuous hydrophilic domain. The template was then removed by calcination. X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy (TEM) were used to characterize the films. Well-ordered spherical domains in the TEM images with a spacing of 15 nm consistent with XRD measurements. XPS data shows that the polymer is removed after calcification.

Due to its high refractive index and convenient electronic band gap, titanium dioxide is of interest for numerous optical and photovoltaic applications. In many cases, thin films of TiO2 films that exhibit large surface area and/or high degrees of order would be enabling for device fabrication. For example, dye sensitized photovoltaic devices require a high surface area. TiO2 films to ensure large contact area with the photactive dye and mesoporous films are ideal for this purpose. Mesoporous titania is typically produced using sol-gel process that involve the cooperative assembly of structure directing agents and alkoxide precursors in solution. Since structure formation and precursor condensation are occur simultaneously, control of long-range order, pore orientation and the fabrication of defect-free, thick films is a challenge. This requires long aging periods for pore formation and allows for little flexibility in template selection since the template and precursor have to be mutually soluble. Recently we reported the new approach to mesoporous silicates that involves the infusion and selective condensation of metal alkoxide precursors within one phase domain of a highly ordered, preformed block copolymer template doped with supercritical carbon dioxide. The template is then removed to produce the mesoporous oxide. Using this approach, we have replicated ordered spherical and cylindrical morphologies to yield robust silica films over 1 micron thick while maintaining all the structural details of the sacrificial copolymer template. Here we extended this approach to the preparation of well-ordered titania films. The template was prepared by spin coating a blend of polystyrene-b-poly(ethylene oxide)132-b-poly(propylene oxide)132-poly(ethylene oxide)132 and poly(4-vinyl phenol) (MW=20,000) with a PEO side chain on a silicon wafer. The polymer blend microphase separates upon drying and the acid catalyst partitions selectively into the continuous hydrophilic domain. The template was then removed by calcination. X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy (TEM) were used to characterize the films. Well-ordered spherical domains in the TEM images with a spacing of 15 nm consistent with XRD measurements. XPS data shows that the polymer is removed after calcification.

2:45 PM AA3.5
Fabrication of Square Microcapsules and their Assembly Behavior. Eun Sook Li, Xavier Bade*, Jan Lamors and John B. Wiley*; 1Department of Chemistry, University of New Orleans, New Orleans, Louisiana; 2Department of Microelectronics and Information Technology, KTH Royal Institute of Technology, SE-164 40 Kista, Sweden.

Micron-sized square tubes and capsules have been fabricated by using a silicon-membrane/collodion-sphere composite as a template. The pores of Si membranes can be formed by a polyelectrolyte nanotubes such that a gap is created along the wall of the channel. Electrochemical deposition within this modified structure creates square metal tubes. The tubes can be released from the membrane, or with further processing, be converted to buoyant microcapsules with interesting assembly properties.

3:00 PM AA3.6
Low Temperature Synthesized Sn Doped Indium Oxide Nanowires. Shu Ji Li*, Chia Ying Lee*, Pang Lin* and Twang Jung Teng*; 1Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 2Electronic Engineering, National Chiao Tung University, Hsinchu, Taiwan.

The selectivity, well controlled and directionally grown Sn doped In2O3 nanowires (In2O3:Sn nanowires, SIO NWs) were synthesized at a low fabrication temperature (~770 oC) through a vapor-liquid-solid (VLS) process under a high purity carrier gas flow. The majority of SIO NWs is grown along [222] with [400] and [440] minority forming directions which implies a nearly epitaxial crystal structure. There are less physical defects such as line or planar defect and contaminations in the SIO NWs through high resolution transmission electron microscopy (HR-TEM) observations. The spectrum of photoluminescence (PL) emission indicates a stable strong blue light peak located at the wavelength of ~400 nm at room temperature. The Sn dopant in the SIO NWs can enhance the conductivity of the nanowires leading to the lowering of the turn-on electric-field to ~0.82 V/um under a current density of up to 2.0 mA/cm2 based on their field emission characteristics. Furthermore, the electric field emission enhancement coefficient is also increased to 1.48*105 which is very close to the carbon nanotubes, (CNTs) level. The low temperature fabricated (~770 oC) SIO NWs exhibited higher field emission area factor and larger field adjustment factor than those values of 900 oC fabricated nanowires, which is due to the Sn dopant that remained more into the nanowires when fabricated at 770 oC. The Sn dopant added in the in SIO NWs is ~2.48 a.t.% which lower the resistance and increase the conductivity, respectively. Therefore, the vertically selectively grown SIO NWs array is a good candidate for the future flat panel display applications.

3:30 PM AA3.7

Today, the extent to which nanoscopic building blocks can be engineered has undergone a quantum increase. We are on the verge of new materials revolution in which entirely new classes of building blocks will be designed and fabricated with desired features, including programmable instructions for assembly[1]. Molecular, nanoparticle, and colloidal building blocks of matter can now be fabricated with anisotropic interactions due to shape, functionalization, or surface patterning. Genetic and molecular engineering of biomolecules and macromolecules has opened up new possibilities for conferring recognition and chemical specificity to inorganic nano building blocks. Principles of self-organization in living systems are being exploited for the assembly of synthetic structures from biologically-inspired building blocks. Yet, little is known about how to control the self-organization of these new building blocks[2] and their fabrication into multifunctional nanomaterials and nanosystems. We seek to develop a theoretical framework for predicting the self-assembled structures that result from nano building blocks patterned or functionalized at the organic or biomolecular level, or to form shape nanoplates(1) including patchy particles(3) and tethered nanoparticles(4,5). In this talk, we present results of molecular dynamics and Monte Carlo simulations of self-assembly of model patterned building blocks, and show how building block shape and topology, pattern anisotropy, and interaction selectivity can be exploited to achieve complex mesoscale one-, two- and three-dimensional structures such as wires, sheets, and shells (2-7). We apply geometric packing rules and discuss their opportunities and limitations for predicting equilibrium structures (6,7). We investigate the interplay between assembly thermodynamics and kinetics and explore transformations between ordered structures under changes in thermodynamic and external fields (8). We further investigate via simulation the stability of assembled structures with respect to various fabrication limitations of the building blocks (9), for nanowires, for nanotubes and nanocomputation. References: (1) S.C. Glotzer, Science 306, 419, 2004. (2) S.C. Glotzer, M.J. Solomon and N.A. Kotov. AIChE J 50, 2249, 2004. (3) Z.L. Zhang and S.C. Glotzer, Nano Lett. 4, 1407, 2004. (4) Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer. Nano Lett. 3, 1341, 2003. (5) E.R. Chan, X. Zhang, C-Y Lee, M. Neurath and S.C. Glotzer, preprint. (6) C.R. Jacovella, M.A. Horsch, Z.L. Zhang, S.C. Glotzer, preprint. (7) X. Zhang, C-Y Lee, F. Qi, J. Kiefer and S.C. Glotzer, preprint. (8) T. Chen, Z.L. Zhang and S.C. Glotzer, work in progress. (9) S.L. Teich-McGoldrick, J. Mucke, Z.L. Zhang and S.C. Glotzer, work in progress. This work is supported by grants from the NSF (CPS-0210551 and DMR-0103389), and the DOE (DE-FG02-02ER46000 and DE-FG02-03ER46004).

4:15 PM AA3.8
Core-Shell Nanoparticles via Surface-Templated Self-Assembly of Block Copolymers on Nanoparticle. Youngjo Kang and T. Andrew Tatonj Chenlistry, University of Minnesota, Minneapolis, Minnesota.

Polymer-coated nanoparticles are useful both because of their improved solubility and stability and also because of their potential in chemical and biotechnological applications. Attaching polymers to nanoparticles typically requires specific chemical bonding between polymer molecules and the nanoparticle surface. We have developed an alternative noncovalent method of encapsulating nanoparticles within crosslinked amphiphilic block copolymer micelles
to form permanent core-shell nanostructures without the need for covalent attachment of the polymer to the particle. As a demonstration of concept, gold nanoparticles were encapsulated within micelles (PS-b-PAA or PMMA-b-PAA) by simultaneously desolvating the hydrophobically modified particles and the hydrophobic polymer block. The resulting core-shell nanostructures were then functionalized by cross-linking the outer hydrophilic block. We demonstrate that the thickness of polymer layer formed around nanoparticles can be programmed by varying either the structure of the copolymer or the ratio of polymer to particles. We find that the optical properties of the encapsulated gold nanoparticles can be also dictated by the molecular characteristics of the assembled copolymers. We anticipate that this encapsulation method will allow researchers to create polymer shells on nanostructured surfaces, effective surface chemistry, and to conjugate these shells with functional molecules.

4:30 PM AA4.9
Self-Assembly of Helical Aromatic Molecules in Multi-Layered Films. Karl-Heinz Ernst1, Manfred Parchasch1 and Roman Fasel2,3; 1Molecular Surface Technologies, EMPA Materials Science and Technology, Duesseldorf, 2H, Switzerland; 3EMP A, Thun, Switzerland.

Highly ordered helical materials are the key devices for circularly polarized electro luminescence (CPEL). Furthermore, the outstanding nonlinear optical properties of chiral films attracted some interest recently. On the other hand, the organic film/electrode interface properties are crucial for the efficiency of organic light-emitting devices (OLEDs). In order to create highly ordered helically structured, well-filmed CPELs, we follow the approach, similar to induction of helicity in nematic liquid crystals, of creating helically structured films of OLED-active molecules, e.g. pentacene, by co-deposition with helical molecules. As the first step, we investigated the layered film optical and chemical properties of the encapsulated gold nanoparticles in water. In order to elucidate the role of various functionalities, e.g. helicity, of the molecule into mesoscopic structural properties, e.g. helicity, of the molecule into mesoscopic structural properties of the nanoparticles. [1] R. Fasel, M. Parchasch, K.-H. Ernst, Angewandte Chemie Int. Ed. 42 (2003) 1777.

4:45 PM AA4.10
Ligand Functionality as a Versatile Tool to Control the Assembly Behavior of Preformed Titania Nanocrystals. Julien Pelleux, Nicola Pina, Markus Antonietti and Markus Niederberger; Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

In addition to the synthesis of nanoparticles with control over particle size, shape and crystal structure, the main focus of nanochemistry research is the assembly/functionalization of nanoparticles more and more towards the use of these nanoparticles as building blocks for the fabrication of 1-, 2- and 3-dimensional superstructures. The synthesis of powders consisting of nanoparticles, which have their assembly behavior already encoded on the surface, would be a key step towards self-assembled controlled fabrication of nanostructures. In this talk we describe a strategy to predict the assembly behavior of anatase nanocrystals. The process is based on the synthesis of surface-functionalized nanoparticles in a nonaqueous procedure, followed by redispersion of the nanoparticles in water. In order to elucidate the role of various functional ligands (the assemblers) adsorbed on the surface of the nanoparticles, we performed detailed investigations on the assembly properties of the nanoparticles in dependence of the ligand functionality. We observed that the nanoparticles can assemble in different fashions, either leading to undefined mono- and polycrystalline aggregates, or to anisotropic nanocrystals of several hundred microns in total length, composed of a continuous string of precisely ordered nanoparticles along the [001] direction [1]. In the latter case, systematic variation of the surface-bound organic assembles reveals that four parameters play a particularly important role. Cationic groups are necessary to disperse and stabilize the nanoparticles in water, i) the surface coverage of the nanoparticles must be above of 40 % as provided by amino di- and trialkylol, ii) the anatase crystal faces present different surface energies possible orientations and iv) the surface reactivity of the different crystal faces towards water allows the specific desorption of the protective ligands [2]. [1] J. Pelleux, N. Pina, M. Antonietti, M. Niederberger, Adv. Mater. 2004, 16, 496; [2] J. Pelleux, N. Pina, M. Antonietti, C. Hess, U. Wild, R. Schlogl, M. Niederberger, Chem. Eur. J. submitted.

SESSION AA4: Nano-Bio Interface
Chair: Ortlin Velev
Wednesday Morning, March 30, 2005
Room 3011 (Moscone West)

8:30 AM AA4.11
Cell-Directed Assembly of The Bio-Nano Interface. Helen Boulikas1, Carlee Ashley2, Eric Carney3, DeAnna Loppert2, Seema Singh2 and C. Jeffrey Brinker1,2; 1Sandia Natl Labs/UNM, Albuquerque, New Mexico; 2Dept of Chemical and Nuclear Eng., University of New Mexico, Albuquerque, New Mexico; 3Biochemistry Department, University of New Mexico, Albuquerque, New Mexico.

The incorporation of living cells into solid-state platforms or devices is important for a diverse range of applications including tissue engineering, array-based drug discovery, bio-sensing, and the powering of microdevices. Here we report a novel cell-directed assembly approach to the 3-D incorporation of Saccharomyces cerevisiae in a uniformly nanostructured inorganic host that maintains cell accessibility, addressability, and viability in the absence of an external fluidic architecture. Using in situ grazing incidence x-ray scattering (GISAXS) along with transmission electron microscopy (TEM) and laser scanning confocal imaging, we investigated how amphoteric polypeptide dendrons direct the formation of ordered biocompatible silica mesoporous materials. We also demonstrate the ability of S. cerevisiae to rapidly and efficiently organize nano-crystals and proteins within their surrounding multifunctional liquid vesicles, suggesting a new general synthetic approach wherein cells direct their self-integration into functional hierarchical/multiscale devices.

9:00 AM AA4.12
Morphosynthesis of Micropatterned Crystals by Controlled Transformation of an Amorphous Phase. Joanna Aizenberg and Yong-Jin Han; Bell Labs/Lucent, Murray Hill, New Jersey.

The ability of biological systems to exert precise control over the shape, size, orientation and hierarchical ordering of inorganic materials is of great interest to chemists and materials scientists, who are beginning to recognize its potential in the development of new synthetic pathways and in the improvement of existing materials. Amorphous calcium carbonate (ACC), one of many polymorphs of calcium carbonate but highly unstable under normal conditions, is often observed in biology, with somewhat enigmatic function, ranging from the structural support to the storage of calcium and carbonate ions for the future precipitation in a more stable crystalline form. In this presentation, we report our experimental results on materials synthesis using the latter biological strategy. We form a patterned transient ACC film on a specially designed organic surface that inhibits the nucleation of the crystalline calcium carbonate phases. Controlled transformation of the ACC film into an oriented patterned calcite crystal is induced by introducing a region in a self-assembled monolayer that serves as a site for oriented nucleation. The mechanisms of phase stabilization and recrystallization into a defect-free crystal, as well as their implication in biomaterialization will be discussed.

9:30 AM AA4.13
Synthesis and Self-Assembly Properties of Acylated Cyclodextrins and Nitrilotriacetic Acid (NTA)-Modified Inclusion Ligands for Interfacial Protein Crystallization. David H. Thompson, Mingkang Zhou, Saubhik Haldar, Joseph Franceschi and Yong-Mok Kim; Department of Chemistry, Purdue University, West Lafayette, Indiana.

Three different beta-cyclodextrins, peryalkylated on the primary hydroxymethyl rim of the cyclodextrin (6-Cn(beta)-CD), and nine
different nitrotriatic acid-modified inclusion ligands (R-NTA) have been prepared and their self-assembly properties characterized. These modifications have been developed for nanoscale template-directed crystallization of histidine-tagged proteins at the lipid-water interface via Ni(II)-NTA ligation. Pressure iso-thermal data suggest that the occupancy of the host sites within the (6-Cn)-beta-CD monolayers vary as a function of the carbamido group density for the unmodified beta-CD host and R guest substituents. Negative-stain TEM experiments show that vesicles are formed upon mild sonication of (6-C10)-beta-CD and (6-C16)-beta-CD in 10 mM TRIS, pH 7.4 buffer. Exposure of (6-C10)-beta-CD to N(epsilon)-adnamantamide-lysine-NTA, Ni(II), and hist-GFP produced crystalline arrays of GFP that were more than 5 molecular layers thick. These results suggest that (6-Cn)-beta-CD forms stable lyotropic phases that may be useful for templating the interfacial crystallization of histidine-tagged proteins or other molecules capable of interacting with the R-NTA guest ligands.

9:45 AM AA4.4
Directed Self Assembly of Virus Based Hybrid Nanostructures. Cengiz Sinan Ozkan1 and Chinglun Tsai2;
1Mechanical Engineering, University of California at Riverside, Riverside, California; 2Electrical Engineering, University of California at Riverside, Riverside, California.

Application of biomolecules in self-assembly has an advantage to produce functional building-block for bottom-up approach in nanofabrication. Well-known unencapsulated viruses such as poliovirus (PV) and tobacco mosaic virus (TMV) were used in our self-assembled nanostructure. Icosahedral PV and cylindrical TMV particles provide different design options for heterostructure assembly along with their well-characterized surface properties and nanoscale dimensions. 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) coupling was applied for covalent conjugation between organic virus capsid and functionalized inorganic nanoparticles such as single-walled carbon nanotubes (SWCNT) or quantum dots (QD). We have demonstrated several building blocks using EDC coupling such as SWCNT with PV particles and carboxylated QDs with TMV particles to form heterostructures in nanoscale self-assembly. By taking advantage of the receptor recognition to its virus counterpart, we have also shown that antibody functionalized nanoparticles (SWCNTs, QDs, and Pt particles) attached only to where the virus counterpart was. In this case, directed and selective hybridization of hetero-nanostructures can make conductive interconnects by metallizing virions with metal particle functionalized antibodies which open an avenue to bio-nanoelectronics.

10:30 AM AA4.4
Biomaterials from Nanocolloids. Nicholas Kotey, Department of Chemical Engineering, Biomedical Engineering and Materials Science, University of Michigan, Ann Arbor, Michigan.

The presentation will review the recent advances in the use of nanocolloids to add new functionalities to biomaterials. Layer-by-layer assembly (LBL) affords preparation of ordered layered structures from virtually unlimited palette of nanocolloids. Photofective multilayer from semiconductor particles were used to NG108*15 neuron precursor cells on them. It was found that light adsorbed in the nanocolloid modified surfaces caused a significant increase in neuronal differentiation. The substrates were used in the development of high density electronic devices using nanoscale patterns.

11:00 AM AA4.4
Self Assembly of Nucleic Acid-Carbon Nanotube Complexes for Scaffolding. Nicholas Strickland1, Yariv Pinto2, Nadrian C. Seeman3, John D. Le4, Yariv Pinto1, Nadrian C. Seeman3, John D. Le4
1Mechanical Engineering, University of California at Riverside, Riverside, California; 2Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

In this paper, we describe self-assembly processing of functional carbon nanotubes using single strand deoxyribonucleic acid (DNA) and peptide nucleic acid (PNA) fragments. Previous research has shown the self-assembly of carbon nanotubes to quantum dots via a simple peptide bonding. Here, we use the DNA and PNA for self-assembly of nanoscale components because of its spatial encoding capabilities which will be eventually useful for the integration of diverse functionalized multicomponent functionalized macromolecules and will be eventually useful for the integration of diverse functionalized multicomponent functionalized macromolecules and will have been functionalized via oxidation to introduce COOH groups at the nanotube ends. Amine functionalized ss-DNA and PNA fragments were attached to the COOH groups via the (1-carboethoxyethylaminocarbonyl)dimethylamino acetyl (EDC) coupling reaction. The resulting heterostructures have been characterized using Fourier transform infrared spectroscopy, Raman spectroscopy, scanning and transmission electron microscopy and energy dispersive spectroscopy. We have used this approach for templating DNA and PNA to biomolecules. This work studies the properties of organic carbon-nanotube-DNA and nanotube-PNA complexes with potential applications in future applications including bioelectronics and sensors.
Two-dimensional magnetic nanowire array was assembled by interact biotin-terminated nanowires with an order gold array, which is lithographically patterned on silicon surface. With additional external magnetic field, the nanowire array can be manipulated and oriented. The assembly of three-dimensional nanowire network was realized by exploiting the shape anisotropy of magnetic segments in multicomponent nanowires. Multicomponent nanowires with rod-shaped magnetic segments align to nanowire axis in the magnetic field and nanowires with disc-shaped magnetic segments align perpendicular to the magnetic field.

11:45 AM **AA5.9**

Molecular Templating of Layered Zirconium Phosphonates: Applications in Dental Restorative Composites.

Benjamin Parmian,1,2 Stephen T. Wellinghoff,2 Paul M. Thompson,2 Richard M. Leine3 and H. Ralph Rawls1;1 Restorative Dentistry, UT Health Science Center, San Antonio, Texas; 2Materials Chemistry, Southwest Research Institute, San Antonio, Texas; 3Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Zirconium offers a significant source of radiopacity in dental composite formulations. However, zirconium oxide particles have historically been difficult to disperse in organofunctional zirconium phosphonates offer an attractive alternative to equiaxied zirconia particles. The direct reaction of phosphonic acids with zirconyl chloride generally results in amorphous zirconium phosphate structures. In this study, novel phosphate precursors are shown to template the growth of ordered platey solids, analogous to functionalized nanoclay, in situ within a thermoplastic host polymer. These nanoplatelet fillers bear organic surface groups that intermingle with a host polymer. The degree of intercalation and exfoliation of the nanoplatelets is characterized. It is anticipated that the resulting hybrid organic/inorganic thermoplastic will maintain significant ductility, and hence fracture toughness, despite having enhanced rigidity over the base polymer. Delivery of hybrid thermoplastic systems to dental repair sites will be discussed.

SESSION AA5: Hybrid and Dissipative Structures

Chair: Douglas Gin

Wednesday Afternoon, March 30, 2005

Room 3011 (Moscone West)

1:30 PM **AA5.1**

Self-assembly of Nanostructured Anisotropic Ion-conductive Materials. Takashi Kato1, Misunumi Yoshih2, Kenji Kishimoto1, Hiyuki Ohno2 and Tomohiro Makii2;1 Department of Chemistry & Biotechnology, The University of Tokyo, Tokyo, Japan; 2Department of Biotechnology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

Self-organization processes of liquid crystals can be used to obtain anisotropic functional materials. Recently, we have reported that 2D or 1D ion-conductive materials have been prepared by macroscopically oriented liquid crystalline or rod-like liquid crystals. These liquid crystals show block structures comprising of oligo(ethylene oxide) or imidazolium moieties. Here we show these two series of nanostructured anisotropic ion-conductive materials. We focus on the role of the oriented functional structures by in situ polymerization of ion-conductive liquid-crystalline (LC) monomers. The design of the LC assemblies forming segregated structures in nanometer scale and the formation of self-organized monodisperse nanodendrites in macroscopic scale are keys for the preparation of polymeric materials with enhanced anisotropic ion conductivities.


2:00 PM **AA5.2**


Fluidity, heterogeneity, and the ability to biospecifically recognize cellular receptors represent three central biophysical characteristics of cellular membranes captured by supported phospholipid membranes. These properties give rise to many self-organizing phenomena at the nanometer length scales. Using recent results from our laboratory, we illustrate these processes in the context of the cooperative dynamics associated with raft-like cholesterol/spingomyelin rich sub-structures during their (1) spontaneous formation via the vesicle fusion process, (2) dissolution by the selective cholesterol-extraction and the detergent treatment methods, and (2)selective chemical transformation such as by spingomyelinesis. Functional consequences of these nanoscale structural reorganizations will be discussed. This work is supported by a grant from Basic Energy Sciences, Office of Science, U.S. Department of Energy and NSF Center for Biophotonics Science and Technology.

2:30 PM **AA5.3**

Mimicking Photosynthesis to Make Functional Nanostructures and Nanodevices. John A. Shelnutt1,2, Zhongchun Wang1, Yujian Song1,3, Craig J. Medforth2 and Ena Pireh3; 1Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; 2Department of Chemistry, University of Georgia, Athens, Georgia; 3Departments of Chemistry and Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; CEEQU/Departamento de Quimica, Universidad de Porto, Porto.

We are mimicking the processes and functional constituents of biological photosynthesis to produce a variety of functional nanostructures. The nanostructures are in some cases analogues of naturally occurring nanostructures and are composed of bioinorganic compounds (e.g., tetrapyrroles). Specifically, nanotubes and other nanostructures composed of porphyrins mimic the light-harvesting and photosynthesis functions of the chloroplast rods and reaction centers of green sulfur bacteria. The porphyrin nanostructures are made by ionic self-assembly (Wang, Z.; Medforth, C. J.; Shelnutt, J. A., J. Am. Chem. Soc. 2004, in press). The nanotubes also have desirable electronic and optical properties, making them suitable for incorporation into electronic and photonic devices. More generally, composite functional nanostructures can be made by using the photocatalytic activity of certain porphyrins in the nanotubes or in other environments to photocatalyze the degradation of hazardous materials. The photosynthetic properties of the nanostructures composed of these photocatalytic porphyrins have been used to synthesize functional nanotube-metal composite systems, which may lead to solar nanodevices in which photovoltaic materials are used as a source of hydrogen fuel. In another approach, by spatially localizing these photocatalytic porphyrins and by using the templating properties of surfactant or porphyrin assemblies, we can grow metal-composite nanostructures of various types. For example, photocatalytic seeding and autocatalytic reduction of platinum, palladium, and gold salts leads to remarkable 2- and 3-dimensional dendritic metal nanostructures. In micellar solutions, spherical metal nanoparticles are obtained. With liposomes as the template, dendritic platinum sheets in the form of thin circular disks or foam-like Pt nanomaterials can be made. Synthetetic control over the morphology of these nanoscale dendrites, sheets, and nanotube-like foams is realized by using photocatalytic tin (IV) porphyrins to conveniently and effectively produce a large initial population of autocatalytic growth centers. The concentration of these initiating seed nanoparticles determines the ultimate average size and uniformity of these novel two- and three-dimensional platinum nanodendrites. This work was partially supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, and by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (DE-FG02-02ER15369). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

2:45 PM **AA5.4**

Polymer Based Nanochannels by Electrokinetics Induced Dynamic Assembly. Changchun Zeng, Shengnian Wang and Liy James Lee; Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio.

Two general approaches have been commonly adopted in creation of nanostructures: "top down" and "bottom up", the former relies on lithographic methods, while the latter utilize the assembly of various building blocks to create functional nanostructures. In this study, we are exploring nanostructures by combining "top down" and "bottom up" approaches. Nanostructures were synthesized in a micro/nano patterned polymer template. The polymer template used include nanoporous membranes made by track etching or sacrificial template imprinting, or nanochannels by lithography. A novel process, "dynamic assembly" was performed to guide formation of nanostructures in the template. Specifically, electrokinetic flows are used to drive precursors into the small features and interconnect the assembly in the micro/nano environment. The assembly of silica was investigated. The strategy to control the growth, orientation and interconnection of the nanostructure will be discussed. This approach provides a general methodology to prepare hybrid nanostructures.

3:30 PM **AA5.5**

Confined Binary Fluids in Temperature Gradients: Pattern Formation due to a Coupling Between Convective and Phase-Separation. Anna Raman, Christopher Pooley and Olga
Using a thermal lattice Boltzmann model, we examine the rich phase behavior that develops when partially miscible fluids evolve in the presence of a temperature gradient, which encompasses the critical temperature, $T_c$. In particular, a binary AB fluid is confined between two plates in a gravitational field. The upper plate is fixed below $T_c$ and, hence, the nearby fluid phase-separates into A-rich and B-rich domains. The lower plate is fixed above $T_c$, and the surrounding fluid travels through a homogeneous phase. A coupling between convection (driven by the temperature gradient) and phase separation gives rise to unique nanoscale pattern formation. A number of regimes are identified: regularly spaced stripes with near zero velocity, steady-state column with convection, the periodic disturbance of these columns, and, finally, chaotic droplets from the upper surface. These results highlight new dynamical behavior in partially miscible mixtures. The findings also reveal how these factors can be manipulated to create dynamically-driven nanoscale structures and, thereby, create materials with unique morphologies, which can provide additional functionality to the final products.

4:00 PM AA5.6
Assembly of Complex Microparticle and Nanoparticle Structures in On-Chip Microdroplet Reactors. Orlyn D. Velev, Jeffrey R. Millman, Suk Tai Chang, Ketan H. Bhatt and Brian G. Prevo; Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

We demonstrate how electrically controlled chips can be used for synthesis and manipulation of new types of particles with advanced structure. The method is based on a technique that allows freely suspended microdroplets or particles to be entrapped and transported with the use of microhydrocarbon droplets. Water and hydrocarbon droplets suspended on the surface of fluorinated liquid are driven by fields created by addressable arrays of electrodes immersed in the oil. Each droplet serves as a microscopic reactor, where the particles are formed by solidification of the carrier droplets. When the droplets contain nanoparticles the evaporation of the liquid leads to mesossegregation of the components and leads to the formation of layered particle crystal structures. Controlled on-chip assembly, drying, encapsulation and polymerization can be used to make amphiphilic supraparticles, polymer capsules and semiconducting microbeads.

4:15 PM AA5.7
Achieving Selective Assembly with Topography and Ultrasonically-Induced Fluid Forces. Sunghwan Jung and Carol Livermore; Mechanical Engineering, MIT, Cambridge, Massachusetts.

A self-assembly technique called templated assembly by selective removal is demonstrated, in which mechanical and chemical forces enable selective assembly of tiny components from fluid. The local topography of the substrate is modified to match the component shapes, increasing the area and magnitude of binding energy between components and their target binding sites. High frequency ultrasound is used to create acoustic streaming flow along the substrate. The flow dislodges components from incorrect binding sites while retaining those in desired complexes. This approach allows selective placement based on differences in component size and shape and can potentially be extended down to the 10nm-100nm scale. The concept, supporting theory, and successful experiments are presented here. Monodisperse 1.6 micron silica microspheres are used as test components. E-beam lithography is used to pattern holes in resist on oxidized silicon substrates. A tinled, isotropic wet etch converts the oxidized silicon substrates. Graphoepitaxy is applied to the cylindrical phase of PS-b-PEP diblock copolymer to overcome the disorder intrinsic to this structure. Two novel results will be presented: (1) alignment of cylindrical polymer domains in confined volumes and (2) extension of this substrate-induced alignment above and beyond the confined volumes.* The capacity of this system to accommodate lithographic defects will also be discussed. Alignment is achieved using lithographically assisted hierarchical self-assembly—a combined top-down/bottom-up methodology. This methodology can be exploited in hybrid hard/soft condensed matter systems for a variety of applications. Funding is acknowledged from the University of Chicago-Argonne National Laboratory Consortium for Nanoscience Research, the NSF-MRSEC at the University of Chicago, and the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences.

4:45 PM AA5.9
Formation of Self-organized Nanowires on ZnO Film Irradiated with Focused Ion Beam. W. Kim, H. J. Shin, B. K. A. Ngoi and S. F. Yu; School of MPE, Nanyang Technological University, Singapore, Singapore.

It is both theoretical and practical interest to understand surface morphological evolution during ion beam bombardment. We irradiated ZnO thin film with Ga+ focused ion beam at various incident angles ($0, 15, 30, 45$ and $60$ degree) and used secondary electron images to observe evolution of nanostuctures on the surface. We report observation of periodic surface rippling at large ion beam incidence angles of $45$ and $60$ degree and provide evidence that the ripples form spontaneously during the focused ion beam irradiation. The ripple orientation is perpendicular to the direction of ion beam projection. The amplitude of ripples increases exponentially with ion dose but the ripple wavelength increases with ion dose following a power law. When valleys of the periodic ZnO ripples is completely sputtered away, the remaining ZnO peaks form nanowires of less than 50 nm in diameter. Important device applications of the aligned ZnO nanowires can be envisaged. The Bradley-Harper model (Bradley and Harper 1988) can be used to explain origin of the self-organized ripple formation: Because of the distribution of the ion energy over the depth below the point of impact, concave regions of the surface are sputtered more rapidly than convex regions, resulting in a surface morphological instability. This roughening effect is opposed by a smoothing effect, typically surface diffusion or viscous flow, which has a different dependence on the wavelength of the morphology.

SESSION AA6: Responsive Materials
Chair: Darryl Sasaki
Thursday Morning, March 31, 2005
Room 3011 (Moscone West)

8:30 AM **AA6.1
Liquid Crystals as Amplifiers of Molecular and Riemannian Interactions at Self-Assembled Interfaces. Nichole Abbott, Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin.

This presentation will report on the use of thermotropic liquid crystals as amplifiers of changes in the chemical functionality and nanoscopic organization of molecules at interfaces. Two examples will be presented. First, the design of interfaces that trigger dynamic and reversible orientational transitions in micrometer-thick films of liquid
crystals in response to specific chemical species (e.g., organophosphonates) will be discussed. Second, inspired by the structure and function of biological membranes, phospholipid-adenyl interfaces of thermotropic liquid crystals will be shown to form the basis of biomimetic interfaces that amplify protein-binding events into spatially patterned, orientational transitions in films of thermotropic liquid crystals.

9:00 AM AA6.2 Polydiacetylene Coatings from Self-Assembled Colloid Solutions for Fluorescence-based Biosensing. Mary Reggy1, Brad Pindzola1, Stephen Hussey1 and Anh Tran Nguyen2;1 Analytical Biological Services Inc., Wilmington, Delaware; 2 Biology Dept., University of Richmond, Richmond, Virginia.

Polydiacetylene (PDA) is a conjugated polymer that can switch from a non-emitting to a fluorescent state in response to environmental changes. PDA acts as a transducer to convert molecular interactions into a discernible signal measurable in the macroscopic world. PDA self-assembled colloids have been formed by polymerization of monomeric diacetylene assemblies such as liposomes, tubules and Langmuir-Blodgett films. These materials have been traditionally used for absorbance based sensing, however, moving to fluorescence detection gives increased sensitivity and allows sensing from PDA deposited on opaque membranes. We have developed PDA coatings deposited on porous filters for use in bio-sensors by conjugation of specific receptors, such as antibodies, to the PDA coating. The coatings are easily prepared by filtration of suspensions of self-assembled diacetylene surfactant colloids to deposit ordered diacetylenes on the filter surface, followed by UV exposure to form the PDA polymers. Furthermore, the coating can be removed from any need to prepare Langmuir-Blodgett films as precursors and allows deposition in 96-well microtiter filter plates for assays. Diacetylene colloid suspensions can be prepared from a wide variety of diacetylene amphiphiles with positively or negatively charged head-groups; it is also possible to include phospholipids and other cell membrane components in the coatings. The amphiphiles form liposomes, ribbons, tubules, etc., depending on the amphiphile structure. We have shown that the variation of the precursor colloid structure affects the coating properties through fluorescence microscopy and dynamic light scattering studies of the precursor solutions and SEM studies of the resulting coatings. Antibodies have been immobilized on the colloidal coatings by conjugation to the surfactant diacetylene colloids and also by reaction with functional groups on the coating surface. We have used enzyme amplified immunosassays to study the effect of the precursor formulation, the method of antibody conjugation, the underlying substrate filter material, and the age of the coating, on antibody presentation at the coating surface. We have prepared coatings with antibodies that show consistent antibody activity over more than three months storage in air. These coated filters can simultaneously concentrate and detect microorganisms through binding of the organisms to the antibodies, which changes the coating emission intensity. We have shown fluorescence detection of E. coli, C. parvum oocysts and B. cereus using PDA-antibody coated filters.

9:15 AM AA6.3 Electronic Spatial and Temporal Control of F-actin Polymerization using Microscale Electrodes. Jan Y. Wong and Nicholas A. Melosh; Materials Science and Engineering, Stanford University, Stanford, California.

The self-organization of G-actin monomers into F-actin filaments and higher order structures is essential for the development and motility of eukaryotic cells. These dynamic processes are regulated spatially and temporally in vivo by various actin binding proteins (ABP) and the concentration of free monomers. However, it is difficult to achieve similar dynamic control for in vitro systems, where F-actin polymerization is usually initiated by increasing the bulk concentrations of certain cations (Mg2+, K+) in solution. We demonstrate a technique of microscale electrodes that locally concentrates divalent cations when a potential difference is applied. This allows G-actin monomers in the vicinity of the electrode to become Mg2+-complexed, with significantly lower critical concentrations for polymerization. Thus, we can electrophoretically activate G-actin monomers and initiate polymerization with spatial and temporal precision. By interfacing this electronic control with optical fluorescence microscopy in a feedback mechanism, it may be possible to control F-actin growth. Such a system could have applications for making accurate measurements of the elasticity and polymerization kinetics of F-actin gels, as well as the manipulation of mesoscale objects. Further spatial control may be achieved through the use of electropatterning with VCA-ArP2/3, which act as nucleation sites for filament growth. This could enable the directed growth of individual filaments as tracks for the transport of nanoscale cargos using myosin motor proteins, as well as the synthesis of hybrid actin-Au nanowires.

9:30 AM AA6.4 Building Intelligent Artificial Systems from Molecular Building Blocks. Yungfen Lu1, Byron Mccague1, Huisheng Peng1, Xuan Li1, Jiebin Pang1, Xiang-Ling Ji1 and C. Jeffrey Brinker2; 1 Tulane University, New Orleans, Louisiana; 2 Sandia National Lab, New Mexico, New Mexico.

Nanoscale materials often show unique and superior physical, chemical, and tribological properties. The promise of nanotechnology is fulfilled when these unique properties are translated into dimensions that devices can use. A significant step towards this goal is the hierarchical assembly of nanoscale building blocks into controlled macroscopic structures. Self-assembly, an approach that utilizes non-covalent interactions to organize building blocks into higher order structures, has emerged as a most promising approach. This presentation will address the design, synthesis and device applications of self-assembled nanostructured materials through responsive self-assembly. Biological systems like cell membranes and chameleon adapt to their surroundings by undergoing reversible structural and functional changes in response to external stimuli. Translation of such natural responses to synthetic systems is of interest for sensors, responsive camouflage, drug-delivery and, more generally, for the development of robust engineering materials with life-like qualities. To date environmentally adaptive synthetic materials have been limited mainly to hydrogels, which, at a critical solubility temperature, pH or ionic strength, undergo reversible phase separation resulting in a large change in volume. Here we report the design of supramolecular amphiphiles and their self-assembly and polymerization to form a new class of adaptive materials that exhibit reversible order-disorder and a chiroptatic transition driven by thermal or electric stimulation. Such dynamic assembly provides systems with responsive, adaptive and self-healing functionality analogous to biology systems.

9:45 AM AA6.5 Preparation and Characterization of Phospholipid Bilayers on Elastomeric Stamps and Their Applications in Micro-Contact Printing. Annapoorna R. Sapuri-Butti, Ravi Chandra Butti and Atul N. Parikh; Applied Science, University of California, Davis, California.

This paper describes the formation and characterization of phospholipid bilayers on topographically patterned elastomeric stamps and their application in micro-contact printing of spatially patterned phospholipid bilayers. The elastomeric stamps were made from poly(dimethyl)siloxane and their surfaces were oxidized using ozone-generating short-wavelength uv radiation. Exposing these stamps to solution of small unilamellar vesicles of phospholipids and their mixtures resulted in the formation of two-dimensionally contiguous, fluid phospholipid bilayers as revealed by epifluorescence imaging and fluorescence recovery upon photobleaching measurements. Applications of these bilayer coated elastomeric stamps in micro-contact printing of lipid bilayers reveal the near-complete transfer of the bilayer in contact regions leaving behind fluid bilayer patches in the elevated regions of the stamp. The study sheds important light on the mechanism of bilayer transfer and highlights key differences in stamping fluid bilayers from the more routine applications of stamping in the creation of patterned bilayers. Furthermore, we illustrate the opportunities afforded by the formation of patterned bilayers on flexible and topographically corrugated elastomeric stamp offers useful opportunities in fundamental studies of membrane structure and dynamics and in the design of novel biosensing platforms.

10:30 AM *AA6.6 Nanostructured Organic Catalysts via Hydrogen-Bond Templating of Polymerizable Lyotropic Liquid Crystal Assemblies. Douglas Qin1,2, Weilin Gu1, Yanjie Xu2, Cory Pecinovsky1 and Jizhu Jin1,2; 1 Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado; 2 Department of Chemical & Biological Engineering, University of Colorado, Boulder, Colorado.

Our research group has shown previously that catalytic organic "analogos" to zeolites and mesoporous sieves can be synthesized by cross-linking lyotropic liquid crystals (LLCs) containing reactive headgroups in nanoporous membranes. One potential problem with this approach is that the incorporated functional group in the starting monomers may not be conductive to LLC behavior, leading to loss of activity. We recently discovered that LLC monomers containing an amide linkage near the hydrophilic headgroup can act as structure-directing agents by "templating" similar molecules with poor mesogenic properties into well-defined LLC phases via intermolecular amide hydrogen-bonding. We have successfully used this LLC H-bond templating approach to synthesize organic monomers containing sulfonic acid headgroups into the inverted hexagonal phase to generate a nanostructured solid acid catalyst, even though the acid monomer has poor mesogenic properties. This appears to be a very
molecules can be readily incorporated into the structure-directing agents. This talk will present the synthesis of these templated materials and their catalytic performance.


This study illustrates the extremely interesting possibility offered by Surface Enhanced Raman Spectroscopy (SERS) to use II-VI quantum dots, grown by molecular beam epitaxy, for detecting biomolecules at very low concentration. Motivated by the SERS sensitivity to very small amounts of material and by our recent illustration of an enhanced Raman sensitivity of molecules adsorbed on III-V semiconductor quantum dots, we seek to extend application of the SERS technique to directly probe the adsorption of biological molecules on II-VI semiconductor quantum dots. Raman spectroscopy is a powerful tool for investigating chemical composition, molecular structure, and local chemical environment. However, the major limitation of conventional Raman spectroscopy is its low signal level and the strong fluorescence background, which is often observed in the spectra. This makes it difficult to obtain Raman spectra of biological samples. The SERS technique, which amplifies the Raman signal by several orders of magnitude, can provide a useful and versatile sensing technique. In our opinion, sensors for biochemical substances with these kinds of sensitivity and selectivity could be very attractive. (1) Lucia G. Quagliano, J. Am. Chem. Soc. 126 (2004) 7363.
particles. However, we will demonstrate that the method allows facile fabrication of nanoparticle coatings with a range of other useful properties. This is particularly true of anodic (AR) films from silica microspheres. Uniform nanocoatings were deposited in minutes directly from aqueous suspensions by convective anodization at very low voltage. No additional substrate or particle preparation is required. The deposition process allows control over the coating thickness, optical properties, and the electric conductance of the films (in the case of the gold nanocoatings). For the gold nanocoatings, ambient deposition (AFD) and a step was used to further tune their electronic, optical, and structural properties. Scanning electron microscopy (SEM) observations and electrical conductance measurements showed that heating leads to a transition from a near-unity to a 30% aluminum insulating structure. The surface plasma resonance peak could be tuned by heating to any value from 800 nm to 555 nm. The control over film structure and optical properties in convective anodization offers an excellent means for making AR coatings from silica particles. The refractive index required for AR materials is difficult to achieve in homogeneous materials (either natural or synthetic), but can be achieved using two-phase or composite films. In a single stage of assembly, reflectance of glass and silicon substrates was easily and reproducibly reduced by up to 75 percent relative to the bare substrates. Microstructural investigations using SEM, AFM, profilometry, and ellipsometry provided good correlations to the observed microscopic optical properties imparted by the silica nanocoatings.

Xudong Wang, Elton Graugnard, Jeffery S. King, Zhong L. Wang and Christopher J. Summers; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The monolayer self-assembly (MSA) of polystyrene (PS) submicron spheres is an effective and economical technique for fabricating patterns on a relatively large scale. Atomic layer deposition (ALD), in which film growth is a cyclic, multi-step process of alternating surface-limited chemical reactions, has been demonstrated to be a powerful technique for fabricating high-quality and multifunctional thin films on various substrates. We report a process that utilizes MSA and ALD for the large-scale fabrication of ordered TiO2 nano-bowl arrays. The technique is based on a self-assembled monolayer of polystyrene spheres, which was used as the template for atomic layer deposition of TiO2. The top half of the TiO2 coated PS spheres were then removed with an ion milling machine. In the final step, the PS spheres left on the substrate were washed away by toluene, resulting in a highly-ordered array of TiO2 nano-bowls. Annealing at 850°C for 2 hours transformed the amorphous film into polycrystalline anatase TiO2. SEM studies showed that the periodic structure of the PS monolayer was well preserved during the entire process. The TiO2 walls are ~25 nm in thickness and no distortion was observed after the PS hemispheres were removed. The nano-bowls exhibit uniform size and orientation, which were not changed after the anealing process. TEM studies confirmed their anatase phase and showed that the TiO2 bowels have a polycrystalline structure with a fairly large grain size, typically ~50 nm. The surface morphology of the resultant functional semiconductors TiO2 exhibits promising applications in solar cell, photocatalytic, photonic crystal and photovoltaic technology. The robust and highly-ordered anatase TiO2 nano-bowl arrays with large surface area are expected to significantly increase the efficiency of surface related phenomena. The bowl size can be adjusted by using different sized PS spheres during the formation of the templates and the fabrication technique could also be applied to different substrates with smooth and hydrophilic surfaces, such as silicon, glass, metals, or even polymers. The nano-bowl arrays have been demonstrated to be useful for selecting particles smaller than their inner diameter and could be a good candidate as a size separator and container for fine particles, or even as a high-capacity carrier such as cells for in situ biological reaction in a proper functional groups. [1] For more information, please visit: www.nanoscience.gatech.edu/zlwang

2:30 PM AA7.4 Si-based Nanoscale Island Array and its Related Nanostructures for Nanoelectronics
1Physics & Materials Science, City University of Hong Kong, Kowloon, Hong Kong; 2Physics, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong.

Porous anodic alumina (PAA) with highly ordered pore arrangement, controllable pore diameter, channel length, and fine insulating property is widely used as a template to grow nanowires or nanotubes since the pioneering work of Signor et al. The self-organizing mechanism to achieve an ordered nanopore arrangement is still a problem and a better understanding is vital to applications such as self-assembled nano-electronic quantum computers. Si-based nano-island arrays were prepared using anodization of Si in 0.3 M phosphoric acid (PAA) by two methods. In the first method, a thick silicon film was deposited onto the surface with a highly ordered bowl array prepared by anodization of an Al foil, followed by the formation of a polycrystalline silicon nano-island array on the surface close to the bowl array after aluminum dissolution. In the second method, porous anodization was performed on an Al thin film on Si and a SiO2 nano-island array was subsequently formed electrochemically. Time-resolved atomic force microscopy (AFM) and photoluminescence (PL) were used to investigate the growth process as well as mechanisms. Two applications of the nanoscale islands are presented. A novel nano-MOS array: metallic carbon nanotube connected with nanowires on SiO2 island array on silicon substrate was fabricated using a Si-based PAA template. The electrical properties were determined by I-V and C-V measurements. The lower work functions of the metal nanowires induced lower band-gap flat-band voltages (VFB) compared to the conventional behavior of MOS. This structure is important for CNTs and PAA template via the self-organized mechanism in nanoelectronics. The second example is Cu oxide nanowire array fabricated on Si-based SiO2 nanoscale islands via nanochannels of a Si-based porous anodic alumina (PAA) template at room temperature under a pulse voltage using copper electrodeposition. X-ray diffraction and photoelectron spectroscopy show that the oxide nanowire is CuO2. The nanowires exhibit a preferential growth direction (111) and are interconnected with the nanoscale SiO2 islands as confirmed by transmission electron microscopy (TEM). The formation of CuO2 is due to the alkalinity of the anodized solution. Expected to be the oscillations of the density and current during the experiment tend to result in a small amount of copper and CuO in the nanowires. The cathodoluminescence (CL) data show that the energy level is larger than the bandgap of CuO2 because of quantum confinement effects.

2:45 PM AA7.5 Conjugated Oligomer Self-Assembly: Correlation between Molecular Architecture, Microscopic Morphology and Optical Properties.
Mathieu Surin1, Philippe Leclere2, Prashant Sonar2, Andrew C. Grimsdale3, Klaus Mullens3, Steven De Feyter3 and Roberto Lazzaroni1; 1Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; 2Max Planck Institute for Polymer Research, Mainz, Germany; 3Laboratory of Molecular Dynamics and Spectroscopy, Katholieke Universiteit Leuven, Leuven, Belgium.

Conjugated materials offer new opportunities as active layers in optoelectronic devices. In particular, fluorene-based oligomers and polymers (PFs) are of major interest, since their blue luminescence offers new opportunities as active materials in optoelectronic devices, in particular to achieve full-color light-emitting diodes. Moreover, those polymers combine high fluorescence quantum yield, good charge transport properties and the ease of controlling the film forming properties via the facio substitution.[1] Understanding and exploiting the relationships between the electronic and optical properties is of paramount importance in order to control the device performances. In this context, we study the microscopic morphology of a variety of fluorene-based oligomers. Tapping-Mode Atomic Force Microscopy (TM-AFM) is used to investigate the microstructural properties of various thin deposits made from these molecules and to understand the results in terms of supramolecular organization, comparisons with molecular modeling simulations of chain assemblies are performed. For fluorene-based systems, we show that self-assembly of compounds substituted with linear alkyl groups leads to regular p-stacks into long nanoribbons. In contrast, aryl-based substituted compounds lead to homogeneous, featureless films due to the steric hindrance imposed by bulky substituents that prevents a dense, regular packing of the molecules into well-defined nanostructures. A clear correlation is established between the degree of order in the deposits and the solid-state photoluminescence properties, which can be useful for lipophilic-applicator liquid crystal applications when the specific interactions between the different segments. Using confocal optical microscopy at the sub-micrometer scale, the characterization of the optical properties of the structures is determined. We also apply an original soft lithographic method to orient the self-assembled nanostructures in a confined space defined by the stamp features.[2] References [1] Neher, D. Macromol. Rapid Commun. 22 (2001), 1365; [2] Surin, M. et al. Chem. Mater. 16 (2004), 994. [3] Siringhaus, H. et al. Science 290 (2000), 2123; Meng, H. et al. Chem. Mater. 15 (2003), 1778. [4] Cavallini, M.; Biscarini, F. Nanoletters 3 (2003), 1209.
Photonic Switches Based on Photo-Optic Periodic Nanostructures. Christopher Bunning, Yoshie K. Runyan, Augustine Urbaš, and V. V. Natarajan. Air Force Research Laboratory, WPAFB, Ohio; 2SAIC, Dayton, Ohio; 3Altona Corp., Dayton, Ohio.

Spatially periodic, two-phase nanocomposites with appreciable refractive index variation lead to the formation of a variety of diffraction transmissive and reflective gratings with application in a number of photonic applications. The ability to modulate this spatially periodic refractive index permits a number of tunable or switchable photonic applications. We report here on the fabrication of multi-dimensional structures whose optical properties can be modulated by selective light scattering in photochromic liquid crystals, or by the addition of solid nanoparticles or nanowires. These photochromic liquid crystals are periodically spaced nanoscale LC droplets that lead to optically transparent structures that exhibit Bragg diffraction properties. Upon illumination with a particular wavelength of light, an inhomogeneous phase change can be induced which modulates the refractive index profile. Control of the two-phase morphology is key to optimising the balance between the incoherent and coherent optical properties. We report here on the static and dynamic optical properties as well as the morphological properties of these photo-optic materials.


Arrays of vanadium oxide nanoparticles with long-range order have been fabricated by pulsed laser deposition in an arbitrary pattern defined by focused ion beam lithography. Interaction of light with the nanoparticles is controlled by the geometrical arrangement as well as by the differing optical properties displayed by the metallic and semiconducting phases of VO2. In contrast to previous VO2 studies, we observe that the optical contrast between the semiconducting and metallic phases is dramatically enhanced not only in the infrared, but also in the visible region, exhibiting size-dependent optical resonances and size-dependent transition temperatures. The collective optical response as a function of temperature is characterized by an enhanced scattering of light as the evolving phase transition. The effects appear to arise because of the underlying mesoscopic properties of VO2, the heterogeneous nucleation underlying the phase transition and the incoherent coupling between the nanoparticles undergoing an order-disorder-order transition. VO2 nanoparticle arrays with controlled size and inter-particle spacing open up new opportunities to study a variety of coherent interactions among nanoparticles, with the added advantage that these interactions can be switched on by the thermally driven metal-semiconductor phase transition in VO2.

Langmuir-Blodgett Technique in the Fabrication and Synthesis of Nanostructured Materials. Hong Yang, Xiaowei Teng, and Qijie Guo; 1Dept of Chemical Engineering, University of Rochester, Rochester, New York; 2Laboratory for Laser Energetics (LLE), University of Rochester, Rochester, New York.

Langmuir-Blodgett (LB) technique has traditionally been used in the thin film deposition of organic monolayer and multilayer on solid substrates. This approach has several advantages in the precise control of thickness and composition of the deposited thin films. In recent years, LB technique has been extended to the fabrication of thin films of surfactant-capped nanoparticles and nanowires. LB technique-based unconventional fabrication approaches of nanomaterials have been developed recently by our and other groups. In this presentation, we will present our recent work on the development of the fabrication of nanostructured arrays using nanoparticles as precursors. To this end, several classes of magnetic nanoparticles including Fe2O3, Pt@Fe2O3 have been used. In particular, magnetic ring arrays can be generated by using a combined LB technique and overpressure contact printing (oCP) method. The use of LB technique as a synthetic tool for making nanostructured materials will be also presented. I will discuss a LB technique-based synthesis of low-dimensional hierarchical nanostructures. These nanostructures and nanomaterials have been characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), electron diffraction (ED), powder x-ray diffraction (XRD), energy dispersive X-ray (EDX), electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Magnetically responsive materials and structures have also been studied using different techniques, such as superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM).

Cadmium Selenide Nanobelts. Christopher Ma, Georgia Institute of Technology, Atlanta, Georgia.

Wurtzite structured Cadmium Selenide (CdSe) in an important II-VI semiconductor compound for optoelectronics. CdSe quantum dots are the most extensively studied quantum nanostructure due to their tunable properties and they have been used as an example for investigating a wide range of nano-scale electronic, optical, optoelectronic, and chemical processes. CdSe was also first example for demonstrating self-assembled semiconductor nanocrystal superlattices. With a direct bandgap of 1.8 eV, CdSe quantum dots have been used for laser diodes, nanosensing, and biomedical imaging. Although CdSe quantum dots have been the dominant material for studying quantum confined effect, there are only a few reports on the synthesis of quasi-one-dimensional CdSe nanostructures. Shape-controlled synthesis of CdSe nanorods, template-assisted synthesis of CdSe nanowires and nanotubes have been demonstrated through electrochemical and chemical approaches. Two-dimensional arrays of CdSe nanowires have been fabricated using e-beam lithography. These nanowires and nanotubes are composed of nano-size grains and they are polycrystalline in nature, thus, the grain boundary scattering could greatly affect the optoelectronic performance. We report the synthesis of single-crystal nanobelts structure of wurtzite CdSe. In addition to controlling the structure of the one-dimensional nanostructure, the properties can also be controlled by controlling the crystallographic growth direction. The wurtzite structured CdSe has an important characteristic, which is the polar surfaces that lead to an asymmetrical growth along the sides of the ribbons, called Spontaneous Polarization-induced Asymmetric Growth (SPA) growth. The growth can cause fingers to grow from the sides. These polar nanostructures have applications ranging from piezoelectric cantilevers to bio-sensor arrays. [1] Chin Ma, Yong Ding, Daniel Moore, Xudong Wang and Z.L. Wang* "Single-Crystal CdSe Nanowires", J. Am. Chem. Soc., 126 (2004) 708-709 (featured by Nature 427 (2004) 497). [2] For more details, please visit: www.nanoscience.gatech.edu/zlwang

SESSION AA8: Poster Session
Chair: Shuhong Yu
Thursday Evening, March 31, 2005
8:00 PM
Salons 8-15 (Marriott)

AA8.1
Controlled Synthesis of CdS Nanobelts and their Optical Properties. Yu Wang, Guozhong Wang, Man-Yan Eric Yau and Dickson H. L. Ng; Dept. of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong.

Cadmium sulfide (CdS) nanobelts were synthesized on an Au-capped Si substrate via chemical vapor deposition (CVD) by sintering CdS powder in a temperature range between 840°C and 1060°C for an hour under a pressure of ~10 Torr. The morphology and microstructure of the nanobelts were characterized by x-ray diffraction (XRD), electron microscopy (SEM) and energy dispersive X-ray (EDX). The nanobelts were further characterized by x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Magnetically responsive materials and structures have also been studied using different techniques, such as superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM).
CdS nanobelts were found on the Si substrate, one was with Au droplet tip and the other without. Based on the size of the Au catalytic site, two models for the growth of these CdS nanobelts were proposed: namely the Au-assisted vapor-liquid-solid tip growth and the Au-assisted base growth. When the size of the Au droplet was smaller than 100 nm, it was lifted by the growing CdS (in tip growth); or CdS nanobelts grew from the droplet when the Au nanoparticle was lifted by the belt (in base growth). The optical properties of the CdS nanobelts were studied by room temperature cathodoluminescence (CL). The CL spectra of the CdS sample sintered at different temperatures exhibited two peaks. One peak was found at ~510 nm, and the other between ~700 and ~756 nm. The first peak corresponded to the intrinsic emission of CdS, while the second one corresponded to the sulfur vacancies in the nanobelts. We found that the ratio of the amplitude of the first peak to that of the second peak decreased gradually from 5:5 to 0.2 as the sintering temperature increased from 880 to 1040°C. Higher sintering temperature induced more sulfur vacancies thus increased the intensity of the deep level emissions. Moreover, a blue shift of 49 nm was also observed for the deep level emission when the sintering temperature was increased by 100°C. It was possible that the sulfur vacancies increased at high temperatures, and the molecules were not entirely the same, and their corresponding deep level energies were slightly different. In this presentation, we report the synthesis and characterization of CdS nanobelts. The growth mechanisms of these nanobelts are proposed. The study of the effect of sintering temperature on their optical properties will also be presented.

**AA8.3**

**From Small Spherical and Thick Rod-Like Molecules Towards a New Class of Amphipatic Polystyrene-based Dendrigraft:**

An Atomic Force Microscopy Study, Pascal Vitrail1, Michel Schoppacher2, Alain Deffieux2, Redouane Borsali1,2, Julien Bernard2, and Roberto Lazzaroni1; 1Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; 2Laboratory of Chemistry of Organic Polymers, University of Bordeaux, Pessac, France.

In this work, comb-like and rod-like polystyrene-based graft copolymers are studied. These copolymers are synthesized by the graft-on-graft polymerization of styrene monomers with specific functionalities using a microfluidic droplet reactor to obtain ‘monomodal’ MIP’s particles with only high affinity receptor sites to achieve high performance molecular recognition function.

**AA8.4**

**Transferred to AA4.0**

**AA8.5**

**Novelty Scale Patterning using Di-Block Copolymer:**

Zuoming Zhao, Tae-Sik Yoon, Wen Peng, Biyun Li and Ya-Hong Xie; Materials Science and Engineering, UCLA, Los Angeles, California.

A new class of amphipatic polystyrene-based dendrigrafts were prepared by incorporating polymerization of the constituting PC EVE and PS sequences of the hyperbranched (PCEVE-g-(PS-b-(PCEVE-g-PS))) copolymer bearing end-functional polystyrene lateral branches. The method is thus a versatile way to create advanced levels. We introduced a molecularly imprinted polymer (MIP) as a promising candidate of the patterning tasks. MIP is a ‘soft’ material. Due to our increasing demands in miniaturization, microfabrication of functional polymers with specific molecular architectures. In addition, the architectural complexity of these molecules and their organization on surfaces is investigated by tapping mode atomic force microscopy (TM AFM). Our AFM measurements demonstrate that the molecules present unimodal and narrow size distribution. As a step further, these molecules can be functionalized by poly(methyl vinyl ether) (PMVE) or poly(ethylene oxide) (PEO) end-chains to prepare new amphipatic species that are promising for drug encapsulation. The synthetic approach used to prepare these new water-soluble species is chain-extension of the external polystyrene branches of the molecules by protected vinyl ethers. Consecutive deprediction of the hydroxyl functions of the vinyl ether units then yields a dendrigratf constituted by a hydrophobic polystyrene core surrounded by a dense poly(vinyl ether) hydrophilic shell. The obtained nano-sized macromolecular structures are fully soluble in aqueous media and also present unimodal and narrow size distribution. The dimensions and shape of the individual macromolecules before and after the deprediction step are investigated in solution using light scattering (elastic SLS and quasi-elastic DLS) and arrested unimolecular deposition using atomic force microscopy and cryo-electron microscopy. The obtained results using both imaging techniques are in agreement with those obtained by SLS and DLS and provide additional information about the structure of the amphipatic dendrigrafts. Both the protected and the deprotected amphipatic polymers exhibit a complex internal organization constituted by distinct subdomains. These peculiar morphologies result from the internal segregation of chemically distinct macromolecular blocks that constitute the dendrigratf branches and associate with neighboring blocks to form separate phases.
A unique composite nanoscale architecture that combines the molecular dynamics of lipid membranes with a corrugated nanotextured silicon wafer was prepared. This is characterized by fluorescence microscopy and scanning probe microscopy. A silicon wafer patterned with a raised line structure of the following dimensions: 100 nm line width, 200 nm line height and a 360 nm pitch, was consecutively coated with a monolayer of membrane. In situ atomic force microscopy (AFM) imaging revealed the membrane to drape over the silicon structure producing a corrugated topology with an amplitude of 40 nm and a pitch matching the underlying silicon substrate. Fluorescence recovery after photobleaching (FRAP) experiments found that on the microscale the membrane lipid exhibited anisotropic mobility coincident with the silicon substructure. These results show that while the lipid membrane maintains much of its self-organizing behavior, the corrugated topology is an additional characteristic of the membrane substructure that influences the dynamics of the molecular motion within the membrane. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

**A8.8 Studies of Single-Molecule Nanostructures Formed by Polyquoinoline Bottles:** Jessica Maryn Hancock, Yan Zhu, Maksudul M. Alam and Samson A. Jenekhe. 1Chemistry, University of Washington, Seattle, Washington; 2Chemical Engineering, University of Washington, Seattle, Washington.

Polymer bottles, also called cylindrical brushes, are macromolecules in which polymer side chains are densely grafted onto a flexible polymer main chain. Single molecules of extensively studied poly(2-vinylpyridine) bottlebrushes, such as polyether side chains with poly(methylene methacrylate) main chains, have been visualized as beautiful worm-like cylindrical nanostructures. To many facres of bottlebrush molecules and conjugated polymers, our group recently synthesized a new series of conjugated polymer bottlebrushes consisting of polybenzyllines pendant side chains of varying chain lengths. The nanostructural, photophysical and electrochemiluminescent properties of this series of bottlebrushes are reported here. Atomic force microscopy and scanning electron microscopy images of the bottlebrushes indicate that the single molecules form cylindrical rodlike nanostructures that are approximately 66 nm in length and 20 nm across. LEDs fabricated from the bottlebrush macromolecules showed enhanced electroluminescence and efficiency compared to identical devices made from the corresponding polyquinoine homopolymer. Our results show that bottlebrush polyquinoines form single-molecule nanostructures with enhanced electronic and optical properties.

**A8.9 One Step Preparation of Hollow Gold Spheres:** Peter J. M. Siong, Galen D. Stucky and Timothy J. Deming; Chemistry, University of California at Santa Barbara, Santa Barbara, California.

Hollow metal spheres are an interesting class of materials due to their peculiar optical properties. Some hollow metal systems have been studied and they are envisioned to be parts of sensors, bandgap materials and cancer treatment agents. Most synthetic methods for metal hollow sphere preparation are based on several steps, which cause many of the prepared shells to be incomplete, cracked, with rough surface and varying shell thickness. Here we describe an easy approach for gold hollow spheres preparation using a one step chemical reduction in aqueous solution at room temperature using polyelectrolyte/polyion spherical aggregates as template. The template generated high local concentration of precursor compounds, leading to localized reduction and formation of a smooth gold metal shell around the template. The hollow spheres are with diameter in the range of 0.8 to 5 μm with thickness varying between 3 and 50 nm which thickness can be controlled by changing the experimental conditions. They are thermally stable and can be isolated in a dry state. Scanning electron microscopy, focused ion beam and transmission electron microscopy examinations show that the hollow metal spheres are very smooth and are not consisting of loosely bound nanoparticles but as a single continuous metal shell.


This paper reports a new methodology for the directed assembly of nanowires based on the use of a genetically engineered molecule composed of a repetitive polypeptide sequence.

**A8.11 Fabrication and Characterization of Epitaxial BiFeO3–BaTiO3 Nanoflake Hybrids using Nanosphere Lithography:** Rian S. Katiyar, Raja S. Vaddapoo and Sudipta Bhattacharya; Department of Physics, University of Puerto Rico, San Juan, Puerto Rico.

Biferroic materials having coupled electric and magnetic polarization properties undergoing structural transitions at elevated temperatures present some potential for applications in information storage, the emerging field of spintronics, and the sensor market. Over the past several years we have witnessed a very encouraging trend in the development of this new generation of materials, which not only have opened up a new era in the advanced device technology but also enriched significantly our understanding of the underlying mechanisms of ferroelectric and ferromagnetism as well. As the demand for higher device-density pushed the existing processing techniques to their limits, ordered nanostructures became welcome for the futuristic multifunctional devices. We have also studied and incorporated these interesting properties at a nanometer level. Self-assembled nanostructures have attracted particular attention in recent years due to their potential applications in economic and versatile patterning of a wide variety of materials at the nanometer scale with tunable array size and density. In this work, template layers were fabricated using self-assembled array of polystyrene spheres (PS) as the mask. Water dispersions of PS spheres with different diameters ranging from 100 to 400 nm were spin coated on SrTiO 3 (100) single crystal substrates and epitaxial SrRuO 3 thin films deposited over SrTiO 3 . The monolayer formation of the template forming spheres on SrTiO 3 was verified using cross sectional SEM and AFM. BiFeO 3 –BaTiO 3 thin films with a thickness range from 50 –100 nm were deposited on these prepared test substrates by pulsed laser deposition technique. The polystyrene template layers were subsequently removed by chemical etching of the sample in dichloromethane at room temperature in an ultrasonic bath for 3 –10 min. The BiFeO 3 –BaTiO 3 nano–islands were then annealed in oxygen at 650 –800 °C for 1 h. X-ray diffraction and transmission electron microscopy studies indicated the formation of crystalline and epitaxial BiFeO 3 –BaTiO 3 on SrTiO 3 and SrRuO 3/SrTiO 3 heterostructures. The characterization of individual nanostructure on conducting substrates with piezo–force microscopy techniques is presented in this report. The feasibility to produce nanostructures with less than 50 nm lateral sizes have been verified in
Patterning plays a very important role in the development of modern technology. A lot of industrial fabrication processes utilize various patterning techniques to create the footprints for the construction of complicated architectures. In the advent of nanotechnology and nanosciences, the development of nano-patterning techniques is one of the most important factors for both industrial and scientific researches. One of the most economic routes for the fabrication of large ensembles of functional nanosystem is to utilize self-assemble to assemble building blocks such as colloids, inorganic and organic nanowires. However, if the functional nanostructures are to be assembled across many length scales within the integrated system, it is necessary to develop new tools for large-scale assembly of nanostructures and manipulation of individual components. Here we report a simple approach to actively control the assembly of inorganic and organic colloidal crystals in the two-dimensional microfluidic networks. Utilizing a combination of electrocapillary forces and evaporation induced self-assembly, it is possible to actively control the self-assembly process of the colloidal nanoparticles forming colloidal crystals inside the two-dimensional microchannel networks. When colloidal crystals are grown in this system, these devices behave as photonic displays. The same approach may be used to grow materials at different reaction conditions, which allows one to study various aspects of colloidal crystal formation and self-assembly processes. Because there are no moving parts in this system and the sample manipulation is achieved by applying electrical voltage, the whole system could be easily scaled up to carry out more complicated tasks.

### AA8.13 Synthesis of Multi-Component Magnetic Nanocomposites from Core-Shell Nanoparticles

Xiawen Teng1, Hong Yang2,3

1Chemical Engineering, University of Rochester, Rochester, New York; 2Department of Chemical Engineering and Laboratory for Laser Energetics, University of Rochester, Rochester, New York.

Multi-component nanomaterials become increasingly important because they possess electronic, optical and magnetic properties that do not exist in single-phased materials. The precise control of both chemical composition and structure at nanometer length scale is essential for the realization of these multi-component magnetic nanostructures. A face-centered cubic (FCC) tetragonal phase FePt-containing inorganic nanocomposites have been made from Pt@Fe2O3 core-shell nanoparticle precursors under H2/Ar atmosphere at the enhanced temperatures. After annealing, multi-component magnetic FCC colloidal crystals were obtained. X-ray diffraction and ultrahigh vacuum-canning transmission electron microscopy (HV-STEM) showed the FCC FePt phase in the annealed core region and fine edge electron-energy-loss spectroscopy (EELS) analysis showed the presence of iron oxide in the shell region. Moreover, by controlling the reaction conditions, various multi-component compositions were observed in crystalline structures and magnetic properties, which have been characterized by X-ray diffraction (XRD) and in magnetic properties by Superconducting Quantum Interference Device (SQUID) magnetometer. Other magnetic core-shell nanoparticles and nanocomposites will also be discussed.

### AA8.14 Fabrication of Azopolymer Photonic Crystals and their Photoinduced Tunable Optical Properties

Jae-Chul Hong, Caey-Ho Park, Chae-nlin Chun and Dong-Yu Kim; Department of Materials Science and Engineering, Georgia Institute of Science and Technology (GIST), Gwangju, 1 Oryong-dong, Buk-gu, South Korea.

During the last decade, photonic crystals which are arrays of dielectric materials with one-, two-, or three-dimensional periodicity have attracted much attention from many researchers. These photonic crystals that can forbid the propagation of the light of the specific wavelength in the photonic band gap region may be useful for lots of applications in photonic and optoelectronic device area. Self-assembled opal and inverse opal structures by using colloidal particles have been attempted as one of the most promising photonic band gap materials. Particularly, inverse opal structures could be modified to enhance optical properties for complete photonic band gap materials. Various polymer inverse opals have also been fabricated for band gap tunable photonic crystals. Photoinduced photonic band gap tuning in the photonic crystals may open up a new way to the fabrication of the high-speed optical switching devices. In this presentation, we demonstrate fabrication of photoresponsive azopolymer photonic crystals embedded with an epoxy-based azobenzene-functionalized polymer colloidal crystals. The porous azopolymer inverse opal structures were prepared by the hydrofluoric acid aqueous solution treatment. The optical stop band of these photonic crystals at the region of infrared light could be tuned to the different wavelength region by the irradiation of excitation wavelength light for azo chromophores. When azobenzene-functionalized organic materials were exposed to light, azobenzene chromophores performed photoisomerization and orientational redistribution. Photo-orientation of azo chromophores caused the index variation of the azopolymer. Photo-orientation of azo chromophores was confirmed by the polarized absorption spectra analysis as a function of the irradiation time. As a result, the photonic band gap of the whole medium was shifted by its effective refractive index change.
dominant at the final stages of the superlattice formation. At a dose higher than $1 \times 10^{12}$ e/cm$^2$ the superlattice structure was destroyed. These two-dimensional and superlattice formation and deformation seem to be independent of dose rate. The kinetic rate equations can describe the initial growth of the voids, and the anisotropic diffusivity of the vacancies explains the superlattice formation. The achieved three-dimensional void superlattice is an important structure in the photonic bandgap application.


Dynamic Bragg diffraction gratings formed via the holographic photopolymerization of monomer/liquid crystal (LC) mixtures have been extensively studied. Multifunctional acrylate formulations containing nematic liquid crystals have been shown to form holographic polymer dispersed liquid crystal (H-PDLC) gratings easily using ultra-violet or visible photoinitiators. Laser wavelengths of 364, 476, 488, 514, 532 and 647 nm have been used for fabricating the gratings. Recently, the use of a thiol-ene based monomer system has been shown to overcome some of the adverse effects like post polymerization, voltage creep, and non-uniform shrinkage as a result of using highly functional acrylate monomers. Previously, Bragg gratings written with thiol-ene systems have been demonstrated using the ultra-violet 363.8 nm Argon ion laser line. Visible reflection colors were observed, but unfortunately, the range of the reflection notch that can be made by angle tuning is restricted to visible range. Photoinitiation using visible laser lines with thiol-ene systems has not been developed to the extent of the availability for Bragg gratings. In this work, we report on a new visible photoinitiator system developed for the formation of H-PDLCs using thiol-ene monomers. Using this new photoinitiator system, reflection notches can be written from visible to infrared regions. Reflection and transmission H-PDLC Bragg gratings formed with visible photoinitiation were shown to perform well in comparison with previous H-PDLC work using thiol-enes in ultraviolet photoinitiation. Also, the visible photoinitiators, it is still possible to create switchable, highly efficient Bragg gratings. The visible photoinitiator system included the photoinitiator and radical generator Titanocene organo-metallic complex (commercially known as Irgacure 784, Ciba-Geigy) along with a radical generating organic peroxide. The role of benzoyl peroxide and the effects of adding Rose Bengal to broaden the absorption range were investigated. In addition, different nematic liquid crystal formulations containing the visible initiator were examined in order to achieve maximum index modulation with minimum scattering. Various visible laser wavelengths (488, 514, 532 nm) were used to explore the visible photoinitiation with reflection Bragg gratings with colors in the visible and the near infrared regions were fabricated with diffraction efficiencies approaching 60%. Transmission gratings with high efficiencies were also written. The gratings were electrically switchable and the morphology studied by transmission electron microscopy. The development of visible photoinitiator systems broadens the range of the reflection notch that can be written, and the availability of inexpensive visible lasers instead of ultra-violet lasers signifies the importance of this development.

### AA8.18 Lipid Bilayer Coated Microspheres as Optical Sensor Materials for Heavy Metal Ions.

A composite architecture of lipid bilayers fused onto glass microspheres has been developed as an optical sensor material for heavy metal ions. The molecularly dynamic lipid bilayer responds selectively and rapidly to specific metal ions via chemical recognition-induced reorganization of the membrane. The recognition sites are from a pyrene-labeled lipid functionalized with a receptor for Cu(II) ion. Binding of Cu(II) causes a change in aggregation of the lipid within the bilayer subsequently producing a change in the excimer to monomer intensity ratio (E/M) of the pyrene. By applying the bilayers onto glass spheres and assembling the spheres into lattices we are able to generate an optical sensor material that is both robust to the environment and reproducible. The structures are influenced by the surface orientation as well as the type of monolayer recognition-micelle towards [011] or [01-1], which are called type-A and type-B respectively. The surfaces under study include regular singular and vicinal (100), (111)A and (111)B - all on one side of stereographic triangle between the (100) and (111) surfaces. While a one-dimensional chain-like ordering of QDs is found on a singular GaAs (100) and on a slightly vicinal GaAs (100), two-dimensional square-like ordering appears on GaAs (111)B, where n is 7, 5, 4 and 3. A small miscut angle toward (111)B does not improve the chain formation, since the miscut orientation is

### AA8.19 Morphological Development at the Interface of Polymer/Polymer Bilayer with in-situ Compatibilizer under Electric Field.

In this study, electric field was applied to reactive bilayer thin films containing poly(methyl methacrylate-co-glycidylmethacrylate) (PMMA-GMA) and polystyrene (PS) with various amounts of in-situ compatibilizer of mono carboxylic acid end-functionalized PS (PS-mCOOH). The fast growing wavelength (Armax) of the interfacial fluctuation under electric field was changed with various amount of PS-mCOOH, because the interfacial tension between PMMA-GMA and PS decreased due to the PMMA-PS. The morphology of the pillars was influenced specially by the roughness from the shape of the polymer formed in the interface. In two reactive bilayers the formation of graft copolymer and the formation of diblock copolymer, the large roughness as well as the reduction of γ made the smaller wavelength. We measured the interface and surface morphology by using atomic force microscope (AFM), optical microscope (OM) and field-emission scanning electron microscope (FE-SEM). We could obtain the size scale of pillar down to submicron by controlling the amount of the in-situ compatibilizer and film thickness. This work is supported by the US Army Research Initiative Program supported by KOSEF.

### AA8.20 Assemblement of Two Different Types of Nanoparticles from Self-Assemblies of Diblock Copolymer Micelles in the Bimodal Size Distribution for Multifunctional Arrays.

In a selective solvent for one of the blocks, diblock copolymers spontaneously form nanometer-sized spherical micelles consisting of a soluble corona and an insoluble core. These micelles can be coated on substrates by dip coating or spin coating, which forms nanosized arrays, which can be used as a template to synthesize nanoparticles or as a lithographic mask to fabricate nanopatterns. We prepared a binary mixture solution of diblock copolymer micelles with two different sizes. Within the condition that the ratio of large and small micelles was below 1:1, the size and number ratios of copolymer micelles in the mixture solution were effectively controlled. From the mixture solution, an ordered self-assembled nanostructure of bimodal micelles was fabricated, in which hexagonally ordered large micelles were surrounded by small micelles. We utilized the ordered self-assembly of diblock copolymer micelles in the bimodal size distribution as a structured template to synthesize two different types of nanoparticles in specific locations. For example, Au nanoparticles were synthesized in the core of large micelles and Pt nanoparticles in the core of small micelles, resulting in an array of Au nanoparticles enclosed by Pt nanoparticles. Moreover, spatial locations of Au and Pt nanoparticles were switched over simply by exchanging the precursors of nanoparticles between the cores of large and small micelles. Therefore, the methodology based on an ordered self-assembly of diblock copolymer micelles in the bimodal size distribution can be applied to various pairs of nanoparticles to generate multifunctional arrays.

### AA8.21 Controlling the (In,Ga)As Quantum Dot Patterns by GaAs Substrate Indexes.

We report on an investigation of self-organized surface ordering of (In,Ga)As quantum dots (QDs) in a GaAs matrix using multi-layered structures prepared by Molecular Beam Epitaxy (MBE). In-situ Reflection High Energy Electron Diffraction (RHEED) and Atomic Force Microscopy (AFM) were used to characterize the surfaces. The structures are influenced by the surface orientation as well as the type of monolayer recognition-micelle towards [011] or [01-1], which are called type-A and type-B respectively. The surfaces under study include regular singular and vicinal (100), (111)A and (111)B - all on one side of stereographic triangle between the (100) and (111) surfaces. While a one-dimensional chain-like ordering of QDs is found on a singular GaAs (100) and on a slightly vicinal GaAs (100), two-dimensional square-like ordering appears on GaAs (111)B, where n is 7, 5, 4 and 3. A small miscut angle toward (111)B does not improve the chain formation, since the miscut orientation is
perpendicular to the natural surface anisotropy of the (100) surface determined by its corrugated (2x4) reconstruction. But the same amount of mismatch (2×1)A indicates partial improvement of the alignment of the QD chain formation as a result of small surface ripples creating an extra anisotropy along the direction of natural (2×4) reconstruction corrugation. On a high index (111)A surface, the uniform nanocrystals collapse to form two-dimensional (2D) clusters of the QDs along and perpendicular to the chains we change. Then we observe a non-uniform distribution of short QD chains on a (111)A surface, and finally corrugated surfaces on (411)A and (311)A with a red shift due to diffusion of QDs on the two-dimensional clusters. In the present study, we have explored several possible experiments to explore the control of lateral ordering using self-assembly techniques for novel device application.

AAS.22 Multi-Scale Modeling of Quantum Dot Synthesis in Microemulsion Templates. Borislava Kostova1, Goorings N. Karanikolos1, Yannis G. Kevrekidis2 and T.J. (Lakis) Mountzias1; 1Department of Chemical and Biological Engineering, University of Buffalo, Buffalo, New York; 2Department of Chemical Engineering, Princeton University, Princeton, New Jersey.

A lattice-based stochastic simulation technique was developed to describe the formation of ZnSe nanocrystals (quantum dots) inside the spherical microemulsion droplets. In this simulation system containing an amphiphilic block copolymer, a polar continuous phase (formamide) and a non-polar dispersed phase (heptane). The stochastic model describes diffusion of diethylzinc molecules, nucleation of ZnSe through a fast reaction between diethylzinc and hydrogen selenide at the nanodroplet surface, as well as diffusion and coalescence of ZnSe clusters leading to the formation of a single nanocrystal per nanodroplet. The simulation is calibrated to real time by using a diffusion-reaction model describing diethylzinc consumption due to a fast interfacial reaction. The motion of molecules and clusters is programmed according to their diffusivity, which is estimated by using the Stokes-Einstein equation. The formation of stable "magic" clusters with close-caged structure is being tracked in the simulations and the predicted size variation of the final particle is recorded. A thermal analysis of cluster-cluster coalescence was performed using a dynamic model describing (1) energy release due to surface area reduction, (2) energy accumulation in the coalescing particles, (3) energy dissipation to the surrounding medium that can lead to evaporation of the droplet and formation of a thin insulating layer of vapor around the particles (Leidenfrost effect), (4) the melting of coalescing particles when their (size-dependent) melting point is reached. The simulations reveal the possibility of melting and recrystallization of nanoparticles, thus explaining the formation of single crystals in a medium that is at room temperature. The detailed simulation results show possible nucleation of quantum dot synthesis process in the experimental system. 4 G.N. Karanikolos, et al., Langmuir, 20(3), 550-553 (2004).

AAS.23 Vapor-Phase Synthesis of ZnSe Quantum Dots and Single-Crystalline Nanorods. Christos Sarigiannidis1, Tzecul Lee1, Athos Petron1 and T.J. (Lakis) Mountzias; 1Department of Chemical and Biological Engineering, University of Buffalo, Buffalo, New York; 2Department of Physics, University at Buffalo, Buffalo, New York.

The vapor-phase synthesis of 2H-VI nanostructures has several advantages over microemulsion liquid-liquid phases, including high material purity, elimination of solvents, high throughput, and better compatibility with existing microelectronics industries operations. Synthesis and surface modification of luminescent ZnSe nanocrystals (quantum dots) were accomplished by using vapor-phase deposition of dimethylzinc/triethylamine adduct with hydrogen selenide gas (both diluted in hydrogen) in a counterflow jet reactor, operating at room temperature and low pressure (120-360 Torr). The two reactants are fed continuously into a cylindrical chamber from separate inlets of a two-dimensional patterned structure with close-caged (In,Ga)As/nanodroplets for the (311)A and (411)A surfaces. These observations suggest many other possible experiments with the purpose of optimizing the quantum dot formation as a result of small surface ripples creating an extra anisotropy along the direction of natural size-dependent melting. The formation of single-crystalline ZnSe nanorods was accomplished via metalorganic vapor-phase epitaxy on Au catalytic seeds, formed by melting thin Au films deposited on Si substrates. Experiments are underway to synthesize highly-nanocrystalline ZnSe nanowires by using electrochemically-formed nanochannel alumina templates placed over Si wafers that have been covered with very thin Au films. The ultimate objective is to develop vapor-phase synthesis routes that allow precise control over size, crystal structure, orientation, and surface functionalization of these nanophase materials to enable applications exploiting their unique optoelectronic properties.

AAS.24 Controlling the Mechanical Properties of Polymeric Thin Films by a Self-Assembled Binary Array of Monodispersed Polymer Nanoparticles. Cheng Yang and Bing Xu; Chemistry, The Hong Kong University of Science & Technology, Hong Kong, Hong Kong.

In this paper, we will report the synthesis of poly(ester-ether) nanoparticles, which are monodisperse and have selected sizes from 35-120 nm. By mixing these nanoparticles that have different sizes and chemical compositions, we generated two or three dimensional binary arrays of them. The volume ratio of the two monodispersed particles defines the shape and size of the microarray, which was converted to a polymeric film by thermal curing. The tolerance between the tensile strength and the patterns of the arrays will be reported.

AAS.25 Surface Plasmon Absorption and Photoluminescence of Self-Organized Au-Nanopeapodded Silica Nanowires. Ming-Shun Hs1, Lu Sheng Hong2, Chang Hua Shen2, Kai-Hien Chen2, Bo Wen Ke3 and Li Chyong Chen2; 1Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan; 2Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan; 3Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Recently, the optical properties of noble metal nanoparticles embedded in the dielectric matrices have received growing interest due to their potential applications in nonlinear optics. In this study, we report the fabrication and optical properties of a peapod type of one-dimensional (1D) composite nanowire which is composed of silica nanowire encapsulated with Au nanoshapes in periodical alignment along the individual nanowire. The novel Au-epapod silica nanowires were synthesized on quartz substrates using Au as catalyst by microwave plasma chemical vapor deposition (MWCVD). Strong surface plasmon absorption has been observed for the composite nanowire using UV-visible absorption measurement and the absorption band was observed to be tailored by the size of Au nanofibers. Furthermore, the luminescence properties have also been characterized using cathodoluminescence (CL), photoluminescence (PL) and photoluminescence light excitation (PLF) measurement. It was found that the composite nanowire exhibited three emission bands at 3.34, 3.02 and 1.93 eV, respectively. The origin of these emission bands will be discussed. A detail growth mechanism of the self-organized composite nanowires will also be addressed in this study.


Nanocapsule multilayer thin films were deposited sequentially by co-deposition of various layered structures such as Au/SiO2/Au/SiO2 as well as BixTe3/Si2Te3. We measured the thermal conductivity, Seebeck coefficient, and electrical conductivity of these two systems before and after bombardment by MeV Si beam. Our experience shows that electronic energy deposition due to ionization in the track of MeV ion beam can cause localized crystalization. In the case of stacked nanolayers, the MeV ion beam produces layers of nanocrystals which cause significant change in both electrical and thermal conductivity of layered structures. These nanocapsule multilayer thin films have a periodic structure consisting of alternating layers where each layer is between 5-10 nm thick. The ultimate objective of this research is to tailor the figure of merit of layered structures used as thermoelectric generators. The film thickness and stoichiometry were monitored by...
Rutherford Backscattering Spectrometry (RBS) before and after MeV bombardment. We used the in-house developed 3rd method thermal conductivity measurement system to measure the thermal conductivity of the multilayer thin films and used the MMR Hall Effect system to measure the electrical conductivity. We will present our findings during the meeting. \* Research sponsored by the Center for Irradiation of Materials, Alabama A&M University and by the AAMURI Center for Advanced Propulsion Materials under the contract number NAG8-1833 from NASA. ** Corresponding author: D. H. A; Tel.: 256-372-8866; Fax: 256-372-5888; Email: ilia@cm.aamu.edu

SESSION AA9: Electronic and Magnetic Behavior of Ferroelectric/Ferrimagnetic Thin Film Nanostructures of Perovskite-Spinel Phases. Haimei Zheng 1, F. Zavaliche 2, 1, Y. Qi 2. 1Materials/Physics, California State University of Fullerton, Fullerton, California; 2Materials Science Engineering, University of Maryland, College Park, College Park, Maryland; 3Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Ferroelectric/Ferrimagnetic Thin Film Nanostructures of Perovskite-Spinel Phases. Haimei Zheng 1, F. Zavaliche 2, 1, Y. Qi 2. 1Materials/Physics, California State University of Fullerton, Fullerton, California; 2Materials Science Engineering, University of Maryland, College Park, College Park, Maryland; 3Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Multiferroic materials with simultaneous ferroelectricity and magnetism have recently attracted considerable attention for their potential applications in scientific and technological fields. In this talk, I will discuss the systematic shape-evolution of gold, silver and platinum nanocrystals (mostly highly symmetric Platonic shapes) with a modified polyol process. By adding surface-regulating polymer and foreign ions, we can readily access the distinct shapes of tetrahedron, cube, and icosahedron, and control their growth with high yield and good uniformity. These nanocrystals have the perfect symmetry for 2- and 3-dimensional packing and therefore could enable the rational tuning of their optical, electrical, and catalytic properties.

Ferroelectric/Ferrimagnetic Thin Film Nanostructures of Perovskite-Spinel Phases. Haimei Zheng 1, F. Zavaliche 2, 1, Y. Qi 2. 1Materials/Physics, California State University of Fullerton, Fullerton, California; 2Materials Science Engineering, University of Maryland, College Park, College Park, Maryland; 3Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

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Ferroelectric/Ferrimagnetic Thin Film Nanostructures of Perovskite-Spinel Phases. Haimei Zheng 1, F. Zavaliche 2, 1, Y. Qi 2. 1Materials/Physics, California State University of Fullerton, Fullerton, California; 2Materials Science Engineering, University of Maryland, College Park, College Park, Maryland; 3Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.
Magnetic Field-Induced Self-Assembly of Co Nanoparticles. 
Guangjun Cheng, Danilo Romero and Angela Hight Walker; Physics, MIST, Gaithersburg, Maryland.

Under the influence of a small magnetic field, Co nanoparticles can assemble into centimeter-long rigid chains in the direction of the applied field in the colloid solution. After the removal of the magnetic field, the magnetic field-induced (MFI) chains assemble into a three-dimensional (3D) compact structure like protein folding. The MFI self-assemblies can be transferred onto Si wafers and TEM grids at different stages for characterization by optical microscopy or transmission electron microscopy (TEM). The crystalline structures of the MFI self-assemblies are probed by electron diffraction and X-ray diffraction (XRD). A superconducting quantum interference device (SQUID) measures the magnetic field-induced ferroelectric properties of Co nanoparticles. The MFI self-assembly may offer an alternative method for magnetic device fabrication.

11:15 AM AA9.8
Fabrication and Ferroelectric Properties of Submicrometer-sized Barium Titanate Ceramic Pillars by Electrophoretic Deposition of Nanocrystalline Particles. 
Maekota Kuwahara, Yong Jun Wu and Juan Li; Applied Science for Electronics and Materials, Kyushu University, Kasuga, Japan.

We have successfully fabricated for the first time ferroelectric barium titanate ceramic pillars of 250 nm in diameter and 600 nm in height on a Pt/Ti/SiO2/Si substrate by an electrophoretic deposition (EPD) method using a suspension of barium titanate nanocrystalline particles (size=10-15 nm). The suspension used for the EPD experiments was prepared by dispersing barium titanate nanocrystals, synthesized by a sol-gel process using a high concentration alkoxides solution (1.0 mol/L), in 2-methoxyethanol under sonication and appeared to be transparent and slightly yellowish. Barium titanate pillars consisting of nanocrystalline particles were made by EPD using the suspension on a Pt/Ti/SiO2/Si substrate with a resist mold formed on it; the resist mold was fabricated by forming a resist film (thickness=1000 nm) on the substrate and then drilling air holes of 300 nm in diameter, arrayed in a hexagonal lattice (lattice spacing=800 nm), in the film using electron-beam lithography. We fired barium titanate green pillars left on the substrate after removal of the resist mold at 600 degrees in centigrade to convert them into ceramic pillars. This firing condition yielded a hexagonal array of barium titanate pillars, giving no significant grain growth (constituent grains’ size was still under 50 nm), no appreciable change in their shape except for shrinkage, and little lattice disordering. Piezoelectric response measurements were carried out for the ceramic pillars obtained using a scanning probe microscopy technique by applying bias voltages up to 80 V (corresponding to an electric field of 1 MV/cm), and it has been confirmed that individual barium titanate pillars fabricated in this study exhibited distinct piezoelectric butterfly curves. Furthermore, a similar butterfly curve and also a clear ferroelectric hysteresis loop were observed for a barium titanate ceramic thin film with a thickness of 600 nm, prepared using the same EPD and firing conditions as those used for pillars; this may prove that the barium titanate ceramic pillars fabricated are definitely ferroelectric. In this paper, we describe the possibility of developing ferroelectric nanometric crystals with a tunable optical function that can be controlled by electric field.

11:30 AM AA9.9
Electric Switching of Cathodoluminescence in ZnO:Mg Nanoparticles-Polymer Structure. 
Genady N. Panshin1,2, Tae Won Kang1, Andrey N. Aleshin3,4, Andrey N. Baranov5, Y.-J. Oh5 and I. A. Khotina6; 1Department of Physics, Quantum-functional Semiconductor Research Center, Dongguk University, Seoul, South Korea; 2Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, Moscow distr, Russian Federation; 3A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russian Federation; 4Nano System Institute and School of Physics, Seoul National University, Seoul, South Korea; 5Thin Film Research Center, Korea Institute of Science and Technology, Seoul, South Korea; 6A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russian Federation.

We report the effect of reversible switching by electric field between blue-green and red cathodoluminescence (CL) in poly(4,4-diphenylene diphénylène), PDPV, mixed with the 12-60 nm size ZnO:Mg particles. We found that the ZnO:Mg-PDPV nanostructures formed on Si-SiO2 substrate with gold electrodes, demonstrate the CL emission maximum in a blue-green region without electric field. Application of positive bias suppressed the blue-green emission and shifted the emission maximum to the red region. The mechanism for the formation of the exited states in the ZnO:Mg particles-PDPV nanostructure implies the presence of the channels of radiative recombination, which can be controlled by electric field.