SYMPOSIUM AA

Dynamic, Self-Organizing Systems in Multifunctional Nanomaterials and Nanostructures

March 28 - April 1, 2005

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* Invited paper

TUTORIAL

Synthesis, Characterization, Self-Assembly and Property of Nanostructures
Monday March 28, 2005
1:30 PM - 5:00 PM
Room 2009 (Moscone West)

This tutorial will focus on the chemical synthesis and structural characterization of both semiconductor and metal nanostructures. It will also briefly cover their properties, as well as their use as building blocks to fabricate functional devices and systems via self-assembly. The tutorial will be organized into the following four lectures:

1. Vapor-Phase Synthesis of Nanostructures
(Z. L. Wang)
2. Solution-Phase Synthesis of Nanostructures
(Y. Xia)
3. Structural Characterization and Properties of Nanostructures
(Z. L. Wang)
4. Self Assembly with Nanostructures as the Building Blocks
(Y. Xia)

Instructors:
Dr. Younan Xia, University of Washington
Dr. Zhong Lin (ZL) Wang, Georgia Institute of Technology

SESSION AA1/S1: Joint Session: Self-Assembly of Magnetic Nanoparticles

Chairs: Dhananjay Kumar and Ralph Nuzzo
Tuesday Morning, March 29, 2005
Room 3005 (Moscone West)

8:00 AM *AA1.1/S1.1

Multi-Component Nanocrystal Assembly: A Route to Multi-Functional Nanomaterials. Christopher Bruce Murray[1] and Elena Shevchenko[2,1]; [1]IBM, T. J. Watson Research Center, Yorktown Heights, New York; [2]Department of Applied Physics and Applied Mathematics., Columbia University, New York, New York.

Collodial 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 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, PbSe, PbS, PbTe and semiconductor quantum dots. Examples of bianry superlattices with AB13, AB2 and AB5 structures will be discussed allow with other potenial structure encorporating 2 distinct types of nanocrystals as the building blocks.

8:30 AM *AA1.2/S1.2

Arrays of Magnetic Nanowires via Block Copolymer Templates. Thomas P. Russell[1] and M. Tuominen[2]; [1]Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; [2]Physics 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 $1x10^{12}$ per square inch. Electrodeposition within the template produces 10nm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanance 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 magnetoresitive 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 on single-domain elements. This work is supported by National Science Foundation Nanoscale Interdisciplinary Research Team, Materials Research Science and Engineering Center and the Department of Energy.

9:00 AM AA1.3/S1.3

From Self-Ordering Towards Imprint Lithography: Large Scale Periodic Nickel and Permalloy Nanowire Arrays. Kornelius Nielsch[1], Woo Lee[1], Ralf B. Wehrspohn[2], David Navas[3], Manuel Vazquez[3] and Ulrich Goesele[1]; [1]Max Planck Institute of Microstructure Physics, Halle, Germany; [2]Department of Physics, University of Paderborn, Paderborn, Germany; [3]Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain.

In this paper, we will analyze the impact of the nanowire arrangement on the total anisotropy of magnetic nanowire arrays and the deviation of the switching fields of individual nanowire inside magnetic arrays for nickel and permalloy nanowire arrays with a disordered, polycrystalline and monocrystalline hexagonal arrangement of the nanowires. Ni and $Ni_{80}Fe_{20}$ is used for the nanowires due to its small magneto-crystalline anisotropy and small magnetic moment which lead to weak dipolar interactions inside the arrays and a large anisotropy resulting from the nanowire shape which en-ables these materials as suitable materials for patterned per-pen-dicular magnetic media. Self-or-dered alu-mina pore channel arrays are used as tem-plates for the fabrication of magnetic nanowire arrays with a perio-dicity of 65 nm (180 $Gbit/in^2$), 100 nm (75 $Gbit/in^2$) and 500 nm (3 $Gbit/in^2$). A nearly per-fect hexagonal arrangement for the columns occurs only inside very narrow process win-dows for periodic distances of 65, 100 and 500 nm, and a degree of pore filling of almost 100% was achieved. In analogy to polycrystallites, the nanowires are hexagonally arranged in domains, which are extended over more than ten lattice periods. We obtain a perfect hexagonal or monocrystalline arrange-ment on a cm^2-scale, when we introduce imprint lithography in the fabrication process of our magnetic arrays. For the disordered arrays the standard deviation of the nanowire diameter is >20% and for the polycrystalline and monoystalline arranged samples <10% and <2%, respectively. We observe that the total magnetic anisotropy increases by either reducing the deviation in nanowire diameter or by improving the ordering of the nanowire arrangement. In the case perfect ordering, we have detected the highest coercivity (1200 Oe) and total anisotropy (100% squareness) reported for a high-density Ni nanowire array with 100 nm periodicity and a column diameter of 30 nm. This work was funded by the German Federal Ministry of Education and Science (BMBF Nachwuchswettbewerb Nanotechnolgie, Grant No. BMBF 03N8701).

9:15 AM *AA1.4/S1.4

Polar-surface Induced Novel Growth Configurations of Piezoelectric Nanobelts. Zhong L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The wurtzite structure family has a few important members, such as ZnO, GaN, AlN, ZnS and CdSe, which are important materials for applications in optoelectronics, lasing and piezoelectricity. The two important characteristics of the wurtzite structure are the non-central symmetry and the polar surfaces. The structure of ZnO, for example, can be described as a number of alternating planes composed of tetrahedrally coordinated O2- and Zn2+ ions, stacked alternatively along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000-1)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. This polar surface gives rise a few interesting growth features. In this presentation, we will focus on a few growth phenomena that are closely related to the polar surface. The growth mechanisms and the explaination about the growth features will be presented. Some details will be given about the analysis of the nanobelt based materials. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 209 (2001) 1947. [2] X.Y. Kong and Z.L. Wang, Nano Letters, 2 (2003) 1625 + cover. [3] Z.L. Wang, X.Y. Kong and J.M. Zuo, Phys. Rev. Letts. 91 (2003) 185502. [4] Nanowires and Nanobelts - materials, properties and devices; Vol. I: Metal and Semiconductor Nanowires, Vol. II: Nanowires and Nanobelts of Functional Materials, edited by Z.L. Wang, Kluwer Academic Publisher (2003). [5] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science, 303 (2004) 1348. [6] Y. Ding and Z.L. Wang, J. Phys. Chem. B, 108 (2004) 12280. [7] Please visit http://www.nanoscience.gatech.edu/zlwang/ for more information.

9:45 AM AA1.5/S1.5

Magnetic Rings: Influence of Asymmetry. Vitali Metlushko[1], U. Welp[2], V. Vlasko-Vlasov[2], G. Crabtree[2], M. Grimsditch[2], N. Zaluzec[2], B. Ilic[3], J. Bekaert[4], V. V. Moshchalkov[4], Y. Bruynseraede[4], Xiaobin Zhu[5], P. Grutter[6], A. Imre[7], G. Csaba[7], G. H. Bernstein[7] and W. Porod[7]; [1]ECE, UIC, Chicago, Illinois; [2]MSD, ANL, Argonne, Illinois; [3]Cornell University, Ithaca, New York; [4]Katholieke Universiteit Leuven, Leuven, Belgium; [5]University of Alberta, Edmonton, Alberta, Canada; [6]McGill University, Montreal, Quebec, Canada; [7]University of Notre Dame, Notre Dame, Indiana.

Recent studies on Co and permalloy rings have shown that a totally flux-closed magnetic vortex state could be stable at remanence. The two chiralities of the 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 microfabrication techniques allow us to produce systematic 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 Nanostructures 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 amphiphilic block copolymer, a polar continuous phase (formamide), and a non-polar dispersed phase (heptane) that forms spherical or cylindrical nanodomains. The controlled synthesis of luminescent ZnSe quantum dots* and single-crystalline nanorods has been demonstrated by reacting diethylzinc, dissolved 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. ZnSe nuclei are formed by the spontaneous 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 biosensors and DNA microarrays. Promising results have been obtained from templated synthesis of CdSe and from ZnSe synthesis in a different class of templates that employ water as the dispersed phase and zinc acetate dihydrate as the zinc precursor.
* G.N. Karanikolos, et al., Langmuir, 20(3), 550-553 (2004).

10:45 AM AA2.2

Characterization of Hexagonal Nanoscale Oligomers and Their Self-Association into Mesoscale Systems. Kwang Sei Oh[1], Tiberiu Fulop[2], Morton Litt[1] and Kathleen Kash[2]; [1]Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio; [2]Department of Physics, Case Western Reserve University, Cleveland, Ohio.

In recent years we have been studying the development of a general way to fabricate nanoscale features or objects by using novel molecular templates as masks for electrodeposition. The idea and challenge is to deposit a regular self-organized array of molecules-ours are cyclic structures, with internal diameters as small as 5 nm-onto a substrate, and then electrodeposit metal or semiconductor nanofibrils within the macrocycles to form a hexagonal nanoporous architecture. Ionically conductive organic templates, rigid cyclic polyimide oligomers containing sulfonate groups were synthesized from linear building block precursors using kinetically-determined cyclization with three main reaction steps, and characterized. The use of an inner cavity for molecular transport is an integral element of nanoarchitectural design. The sulfonate groups promote the absorption of water and ionic salts. The internal cavities are large enough to allow relatively free ion diffusion. Dynamic light scattering (DLS) demonstrated that the macrocyclic hexamers self-associate strongly to form large aggregate structures in solution at room temperature; the association behavior depends on concentration. A strategy for hexagonal oligomer manipulation for use involves self-organization with the formation of large area molecular templates arranged hexagonally at surfaces. Concentration-dependent morphologies were observed using transmission electron microscopy (TEM). They self-associated, generating supramolecular arrays of hexagonal liquid crystals that were physisorbed on a planar surface. Molecular resolution images of these superstructures were recorded at room temperature using scanning tunneling microscopy (STM). Two types of deposition were observed. The first is a discrete, close-packed honeycomb when the molecules self-assemble on a graphite surface. The second form consists of nanofibrils of about 6 nm diameter; these were observed both as single tubes, or associated into oriented aggregates. Open framework honeycombs supported on a conducting substrate can be considered as large nanopatterned arrays. Their hexagonal channels can be used as prefabricated templates for semiconductor quantum dots or wires, high surface electrodes, etc. We have been able to electrodeposit InSb into the channels and then remove the polymer, getting a hexagonal array of templated nanofibrils.

11:00 AM AA2.3

Single Crystal Silver Nanoparticles with Well-Controlled Shapes. Benjamin J. Wiley, Jingyi Chen and Younan Xia; Univ. of Washington, Seattle, Washington.

High yields of single crystal silver nanoparticles were synthesized for the first time in solution through the addition of chloride to a standard polyol synthesis. The shapes of these nanoparticles were 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. Taking advantage of their extremely high extinction coefficient in the near-IR (800-1000nm, 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.

11:15 AM AA2.4

Dendritic Platinum Nanostructures. Yujiang Song[1,2], Donovan Pena[1], William A. Steen[1], Jennifer L. Pincus[1], Darryl Y. Sasaki[1], James E. Miller[1] and John A. Shelnutt[1,3]; [1]Biomolecular Materials & Interfaces Department and Ceramic Process & Inorganic Materials Department, Sandia National Laboratories, Albuquerque, New Mexico; [2]Chemical & Nuclear Engineering Department, The University of New Mexico, Albuquerque, New Mexico; [3]Department 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, biosensors 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. Herein, we describe a method of synthesis that leads to nano-scale circular dendritic sheets and foam-like platinum nanospheres by chemical reduction of aqueous metal complex with ascorbic acid in the presence of liposome template. The nanomaterials 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 initial population of catalytic growth centers, which resulted in uniform size of nanostructures. These nanomaterials have potential applications, such as catalysis and sensors, due to their high surface area and self-supporting characteristics. 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.

11:30 AM AA2.5

The Preparation and Characterization of Mesostructured Thin Films of Perovskites and Ternary Oxides. Bernd Smarsly[2], David Grosso[1], Torsten Brezesinski[2], Cedric Boissiere[1], Markus Antonietti[2], Clement Sanchez[1], Heinz Amenitsch[3] and Pierre-Antoine Albouy[4]; [1]Chimie de la Matiere Condensee, Universite Pierre et Marie Curie, Paris, France; [2]Colloid Chemistry, MPI of Colloids and

Interfaces, Potsdam, Germany; [3]Institute for Biophysics and X-ray Structure Research, Institute for Biophysics and X-ray Structure Research, Graz, Austria; [4]Laboratoire de Physique des Solides, Universite Paris-Sud, Orsay, Austria.

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 ternary oxides have not been available. Here were 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 (dieletric SrTiO3, ferroelectric LiTaO3). Starting from metal chlorides or alkoxides, thin mesostructured films are dip-coated, the mesostructured being established through a novel type of block copolymer template. Afterwards, a suitable 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 nucleati In order to find an appropriate nucleation procedure, detailed in-situ combined Grazing Incidence Small-angle X-ray scattering (GISAXS) and Wide-Angle X-ray Scattering (WAXS) studies were performed on these materials at the Synchrotron facility at Ellettra (Trieste, Italy). By monitoring the crystallisation and mesostructure changes at the same time, the temperature could be adjusted to obtain thin films with perovskite nanocrystals 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-metal-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. 1 Smarsly et al. Chem. Mater. 2004, 16, 2948. 2 Grosso, D., Boissiere, C.; Smarsly, B.; Brezesinski, T.; Pinna, N.; Albouy, P. A.; Amenitsch, H.; Antonietti, M; Sanchez, C. Nature Material, 2004.

11:45 AM AA2.6
Evolution from Nanowires to Combs and Sheets in ZnO with Controlling Oxygen Partial Pressure. Jae-Hwan Park, Jae-Gwan Park and Young-Jin Choi; Korea Institute of Science and Technology, Seoul, South Korea.

Bottom-up approaches to nanoelectronics using nanoscale building blocks such as quantum dots, nanowires, and nanotubes have received considerable attention to date. However, the feasibility of realizing highly integrated functional devices is still questionable due to the difficulties in the alignment and assembly of the building blocks. In this regard, creation of new types of nanostructures of various sizes and shapes would be of interest. Here, we are reporting on the nanowires, combs, and sheets in ZnO with controlling oxygen partial pressure. Especially, we report "seeable and touchable" ultrawide ZnO nanosheets which can be easily manipulated by conventional lithography and/or assembly techniques, maintaining nano-sized features.

SESSION AA3: Building Blocks and Novel Structures II
Chair: Hong Yang
Tuesday Afternoon, March 29, 2005
Room 3011 (Moscone West)

1:30 PM *AA3.1
Perfect and Nearly Perfect Nanoconstruction Sites for Polyfunctional Nanoparticles and Nanocomposites from Silsesquioxanes. Richard M. Laine[1,2], Mark Roll[2], Michael Z. Asuncion[2], Chad Brick[3], Santy Sulaimann[2] and Tamaki Ryo[1]; [1]MSE, University of Michigan, Ann Arbor, Michigan; [2]Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan; [3]Chemistry, University of Michigan, Ann Arbor, Michigan.

Octafunctional cubic silsesquioxanes [RSiO1.5]8 are unique molecules wherein the body diagonal of the single crystal silica core is 0.5 nm and each functional group at-tached to the vertices of these cores occupies a different octant in Cartesian space. These materials are easily accessible in high yields from simple starting materials including rice hull ash. Furthermore, an extensive variety of functional groups can be introduced. Con-sequently, these materials offer unique opportunities to engineer new types of nanobuild-ing blocks and polyfunctional materials. The nanobuilding blocks provide the tools for creating new types of nanocomposites nanometer by nanometer in one, two or three di-mensions. The polyfunctional materials have unique properties in their own right. We describe here new methods of making and processing highly perfect nanostruc-tures from Q8 [RSiMe2SiO4]8 and T8 [RPhSiO1.5]8 systems and some of their properties including unusual photoluminescence behaviors.

2:00 PM AA3.2
Fabrication of Ordered Titania Films by the Three-Dimensional Replication of Block Copolymer Templates in Supercritical Carbon Dioxide. David Michael Hess and James J. Watkins; University of Massachusetts at Amherst, Amherst, Massachusetts.

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, the preparation of robust, mesoporous 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 to ensure large contact area with the photoactive 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 preparation 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 oxide precursors within one phase domain of a highly ordered, preformed block copolymer template dilated 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 extend this approach to the preparation of ordered titania films. The template was prepared 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 PTSA acid catalyst onto 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 exposed to a solution of supercritical carbon dioxide and titanium diisopropoxide bis(acetylacetonate) at 130 bar and 60oC resulting in precursor condensation within the hydrophilic domain. The template was then removed by calcination. X-ray diffraction (XRD), x-ray photoelectric spectroscopy (XPS), Raman spectroscopy, and transmission electron microscopy (TEM) were used to characterize the films. Well-ordered spherical domains were apparent in the TEM images, with a d-spacing of 15 nm consistent with XRD measurements. XPS data shows that the polymer is removed after calcination.

2:15 PM AA3.3
Ordered Binary Superstructures of Nanoparticles. Elena V. Shevchenko[1,2], Dmitri V. Talapin[1], Stephen O'Brien[2] and Chris B. Murray[1]; [1]T. J. Watson Research Center, IBM, Yorktown Heights, New York; [2]Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York.

The monodisperse nanocrystals can self-assemble into one-, two- and three-dimensional superstructures forming superlattices with high packing density (ccp or hcp). Potentially, the mixtures of nanoparticles can constitute a much richer self-assembled structures. Co-crystallization of binary colloidal mixture leads to the formation of a superlattice which exhibits a high degree of internal order and can be assigned to a certain type of crystalline structure. Monodisperse colloids of crystalline semiconductor, oxide and metal nanoparticles with sizes tunable from $\sim$3 nm to $\sim$17 nm were synthesized via optimized solution phase syntheses. Nanoparticles with different functionality were used as building blocks for the formation highly ordered binary structures. We carried out a systematic investigation to define the conditions favourable for the formation of ordered binary structures. Perfectly ordered binary arrays of nanoparticles were formed on extended areas (up to ca. 6 square microns) upon controlled evaporation of solvent. Upon self-assembly of nanoparticles into a binary superlattice, they must meet the requirement of certain geometrical principles. Murray and Sanders postulated that the formation of a stable binary assembly is possible only if its packing density exceeds the packing density of single-component crystals in ccp or hcp structure (i.e., 0.7405) [1]. However, our experimental results demonstrate the possibility of formation of structures with lower densities. For semiconductor, metal and metal oxides nanoparticle binary mixtures we demonstrate the examples of both dense binary assemblies such as AlB2 or NaZn13 type structures and a variety of more diluted ordered arrays with crystalline structures of CaCu5, AuCu, MgZn2, Fe4C, etc. The effect of nanocrystal size, different stabilizing agents, nanocrystal concentrations, solvents and temperature on the self-assembly in binary mixtures will be discussed. [1] M. J. Murray and J. V. Sanders Phil. Mag. A. 1980, v. 42, p. 721.

2:30 PM AA3.4

Fabrication of Square Microcapsules and their Assembly Behavior. Feng Li[1], Xavier Badel[2], Jan Linnros[2] and John B. Wiley[1]; [1]Department of Chemistry, University of New Orleans, New Orleans, Louisiana; [2]Department 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/colloid-sphere composite as a template. The pores of Si membrane are first modified with a polystyrene nanospheres 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.

2:45 PM AA3.5

Low Temperature Synthesized Sn Doped Indium Oxide Nanowires. Seu Yi Li[1], Chia Ying Lee[2], Pang Lin[1] and Tseung Yuen Tseng[2]; [1]Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; [2]Electronic Engineering, National Chiao Tung University, Hsinchu, Taiwan.

The selective, 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 precise 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 ~440 nm while the excited wavelength is 275 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/cm$\hat{2}$ based on their field emission characteristics. Furthermore, the field emission enhancement coefficient is also increased to 1.48*10$\hat{5}$ 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 ~2.45 a.t.% which lower the resistance and increase the conductivity, respectively. Therefore, the vertically and selectively grown SIO NWs array is a good candidate for the future flat panel display applications.

3:30 PM *AA3.6

Design Rules from Computational Nanoscience for Self-Assembly of Patterned Nano Building Blocks: Insights from in Silico. Sharon C. Glotzer, Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Today, the extent to which nanoscopic building blocks can be engineered has undergone a quantum leap. 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 nanostructures. We seek to develop a theoretical framework for predicting the self-assembled structures that result from nano building blocks patterned or functionalized with organic or biomolecular handles or tethers to form shape amphiphiles(1) including patchy particles(3) and tethered nanoparticles(4-7). 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, junctions 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 applications to nanoelectronics 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, 2978, 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. Neurock and S.C. Glotzer, preprint. (6) C.R. Iacovella, M.A. Horsch, Z.L. Zhang and S.C. Glotzer, preprint. (7) X. Zhang, E.R. Chan, F. Qi, J. Kieffer and S.C. Glotzer, preprint. (8) T. Chen, Z.L. Zhang and S.C. Glotzer, work in progress. (9) S.L. Teich-McGoldrick, J. Mukherjee, Z.L. Zhang and S.C. Glotzer, work in progress. This work is supported by grants from the NSF (CTS-0210551 and DMR-0103399), and the DOE (DE-FG02-02ER46000 and DE-FG02-03-ER46094).

4:00 PM AA3.7

Fabrication of Supraparticles, Janus Microparticles and Microlens Arrays with the Gel Trapping Technique. Vesselin N. Paunov and Olivier J. Cayre; Department of Chemistry, University of Hull, Hull, North Humberside, United Kingdom.

Particles with asymmetric shapes that can be used to make crystals with novel optical properties have attracted much attention in recent years. We have shown that the Gel Trapping Technique (GTT) can be used to asymmetrically coat colloidal monolayers creating so-called 'Janus' particles, after the two-faced Roman god of doors. Partially embedded monolayers of monodisperse polystyrene microparticles in polydimethylsiloxane (PDMS) were used to coat the exposed particle surface with gold, resulting in particles with two 'faces'. The technique is relatively simple and could easily be used to make a variety of Janus particles. Monodisperse polystyrene microparticles are spread at a water-oil interface and super long range repulsion between particles adsorbed at the interface leads to a near perfect hexagonal lattice. The water contains the gelling polysaccharide gellan which, on cooling, forms a gel that traps the monolayer and the oil layer may then be removed without disturbing the particles. Pouring liquid PDMS over the gel followed by curing leads to the formation of a partially embedded monolayer trapped within the PDMS resin which can be peeled away from the gel. To make the Janus particles the trapped polystyrene particles were 'half-coated' with gold. Use of particles of different contact angles allows the creation of monolayers with varying degrees of entrapment of the polystyrene particles within the gel and thus to different degrees of coverage on their surface. At certain conditions we have successfully molded the particle monolayer together with its gelled meniscus around the particles which produced 'flying saucer particles' where the polystyrene particles are surrounded by a ring of gellan. Stretching the PDMS releases the trapped particles and the PDMS films produced, with an ordered array of microholes, could have interesting potential applications as filters or antireflective coatings. By further replicating the microhole array with a photopolymer we produced hexagonally ordered microlens arrays where the lattice constant is fixed by the amount of particles spread at the initial liquid surface. We also used the same Gel Trapping Technique as a novel method for determining the contact angle of particles adsorbed at air-water and oil-water interfaces. The trapped particles have been imaged on the surface of the PDMS replica with SEM. The particles position with respect to the air-water interface or the oil-water interface has been determined from the SEM images of the PDMS replica which gives information for the particle contact angle at the liquid interface. Particle samples of different size and surface chemistry have been examined. We present results for the particles contact angles at air-water and decane-water interface obtained for sulfate latex particles, hydrophobized silica particles, gold particles and polymer microrods.

4:15 PM AA3.8

Core-Shell Nanoparticles via Surface-Templated Self-Assembly of Block Copolymers on Nanoparticle. Youngjong Kang and T. Andrew Taton; Chemistry, University of Minnesota, Minneapolis, Minnesota.

Polymer-coated nanomaterials are useful both because of their improved solubility and stability and also because of their potential in chemical and biotechnological applications. Attaching polymers to nanomaterials typically requires specific chemical bonding between polymer molecules and the nanoparticle surface. We have demonstrated 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 this 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 permanently fixed by crosslinking 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 and chemical 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 nanomaterials that lack effective surface chemistries, and to conjugate these shells with functional molecules.

4:30 PM AA3.9

Self-Assembly of Helical Aromatic Molecules in Multi-Layered Films. Karl-Heinz Ernst[1], Manfred Parschau[1] and Roman Fasel[2,1]; [1]Molecular Surface Technologies, EMPA Materials Science and Technology, Duebendorf, ZH, Switzerland; [2]EMPA, Thun, Switzerland.

Highly ordered helical materials are the key to devices for circularly polarized electroluminescence (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 films for CPEL, 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 structures formed after deposition of heptahelicene ([7]H), a helically shaped polyaromatic hydrocarbon (C30H18), on single crystal metal surfaces. The molecules were deposited in-vacuo via molecular beam technique and the film structures have been characterized with scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD). If an equimolar (racemic) mixture of both helicities (enantiomers) is used on a copper(111) substrate, a separation of the enantiomers is observed in the second layer, while the first layer forms racemic two-dimensional crystallites. From the third layer on, enantiopure multilayered island-growth is observed. Slight changes of the ratio between the left and right handed molecules have a strong influence on the multilayer crystallography. This is due to a change in morphology in the first layer and due to the different epitaxial growth behavior. The pure enantiomers transfer their molecular helicity in the first layer into supramolecular spiral structures [1] and grow also into 3D crystalline islands on top of the closely-packed the second layer. The results will be discussed in the light of transfer of structural properties, e.g. helicity, of the molecule into mesoscopic structures of the films. [1] R. Fasel, M. Parschau, K.-H. Ernst, Angewandte Chemie Int. Ed. 42 (2003) 5177

4:45 PM AA3.10

Ligand Functionality as a Versatile Tool to Control the Assembly Behavior of Preformed Titania Nanocrystals. Julien Polleux, Nicola Pinna, 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 more and more shifts 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 an immense step forward toward the controlled bottom-up fabrication of nanostructures. In this talk we describe a strategy to predetermine the assembly behaviour of anatase nanocrystals. The process is based on the synthesis of surface-functionalized nanoparticles in a nonaqueous procedure, followed by redispersion of the nanopowders 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 building blocks 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 nanostructures of several hundreds of nanometers 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 assembler molecules shows that four parameters play a particularly important role: i) the presence of a terminal amino group is necessary to disperse and stabilize the nanoparticles in water, ii) the surface coverage of the nanoparticles must be above of 40 % as provided by amino di- and trialcohols, iii) the anatase crystal faces present different surface energies which makes possible oriented attachment and iv) the surface reactivity of the different crystal faces towards water allows the specific desorption of the protective ligands [2]. [1] J. Polleux, N. Pinna, M. Antonietti, M. Niederberger, Adv. Mater. 2004, 16, 436. [2] J. Polleux, N. Pinna, M. Antonietti, C.Hess, U.Wild, R.Schlogl, M.Niederberger, Chem. Eur. J submitted.

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

8:30 AM *AA4.1

Cell-Directed Assembly of The Bio-Nano Interface. Helen Baca[2], Carlee Ashley[3], Eric Carnes[2], DeAnna Lopez[2], Seema Singh[2] and C. Jeffrey Brinker[1,2]; [1]Sandia Natl Labs/UNM, Albuquerque, New Mexico; [2]Dept of Chemical and Nuclear Eng., University of New Mexico, Albuquerque, New Mexico; [3]Biochemistry 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 nanodevices. Here we report a 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 small angle x-ray scattering (GISAXS) along with transmission electron microscopy (TEM) and laser scanning confocal imaging, we investigated how amphiphilic phospholipids direct the formation of ordered biocompatible silica mesophases in the absence or presence of S. cerevisiae. We find that living S. cerevisiae alter profoundly the self-assembly pathway, each cell creating around itself an extensive multilayered phospholipid vesicle that interfaces coherently with the nanostructured silica host, and the cells, collectively, switching the nanostructured silica from a hexagonal to a lamellar mesophase. Using yeast genetically-modified to express green fluorescent protein in response to an external stimulus (along with other viability probes), we show that this novel cell-directed hierarchical structure serves as a useful, physiologically relevant standalone environmental sensor. We also demonstrate the ability of S. cerevisiae to rapidly and efficiently organize nano-crystals and proteins within their surrounding multilayered lipid vesicles, suggesting a new general synthetic approach wherein cells direct their self-integration into functional hierarchical/multiscale devices.

9:00 AM *AA4.2

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 of 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 biomineralization will be discussed.

9:30 AM AA4.3

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 Franses and Jong-Mok Kim; Department of Chemistry, Purdue University, West Lafayette, Indiana.

Three different beta-cyclodextrins, peralkylated on the primary hydroxymethyl rim of the cyclodextrin ((6-Cn)-beta-CD), and nine different nitrilotriacetic acid-modified inclusion ligands (R-NTA) have been prepared and their self-assembly properties characterized. These modular amphiphiles have been developed to promote two-dimensional crystallization of histidine-tagged proteins at the lipid-water interface via Ni(II)-NTA ligation. Pressure-area isotherm data suggest that the occupancy of the host sites within the (6-Cn)-beta-CD monolayers vary as a function of the known host-guest binding constant 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-C16)-beta-CD monolayers to N(epsilon)-adamantamide-lysine-NTA, Ni(II), and his6-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 Ozkan[1] and Chunglin Tsai[2]; [1]Mechanical Engineering, University of California at Riverside, Riverside, California; [2]Electrical 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 unenveloped viruses such as poliovirus (PV) and tobacco mosaic virus (TMV) were used in our self-assembled nanostructure. Icosahedral PV and cylindrical TMV particles provides different geometric options for heterostructure assembly along with their well characterized surface properties and nanoscale dimensions. 1-Ethyl-3-(3-dimethyl aminopropyl)-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 heterojunctions 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 be implemented. While using viruses as linkers, we can selectively make conductive interconnects by metallizing virions with metal particle functionalized antibodies which open an avenue to bio-nanoelectronics.

10:30 AM *AA4.5

Biomaterials from Nanocolloids. Nicholas Kotov, 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. Photoactive multilayer from semiconductor particles were used to NG108*15 neuron precursor cells on them. It was found that light adsorbed in the nanoparticle layers results in the electrical excitation of the neurons making this system a functional analog of retina. Assemblies of clay-polymer systems demonstrated exceptional toughness similar to that observed in bones. Similar coiling of the macromolecules on the inorganic surfaces was identified as a structural basis for the functional analogy of clay multilayers and laminar bones and mother-of-pearl. Magnetic multilayers have been used to impart magnetostrictive properties to stem cell scaffolds made from inverted colloidal crystals. The last example of the LBL assemblies with biological functionalities will describe the preparation of basal membranes from collagen and other nanocolloids. Molecular sieving properties of collagen membranes makes them close analog of kidney basal membranes. Layered nanocomposites represent an exceptionally versatile tool for production of biomaterials with novel applications derived from unique properties of nanostructured matter.

11:00 AM AA4.6

Self Assembly of Nucleic Acid-Carbon Nanotube Complexes for Nanoelectronics. Cengiz Sinan Ozkan[1] and Xu Wang[2]; [1]Mechanical Engineering, University of California at Riverside, Riverside, California; [2]Chemical 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 make use of 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 devices. During self assembly, first multiwalled carbon nanotubes 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-ethyl-3-dimethylaminopropyl) carbodiimide HCl (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 also conducted platinum metallization of DNA and PNA fragments to study the properties conductive biological linkages to inorganic components. The metallized nanotube-DNA and nanotube-PNA complexes have potential applications in future applications including nanoelectronics and sensors.

11:15 AM AA4.7

Templated Growth of Metallic Nanowire Arrays by 2D DNA Scaffolding. John D. Le[1], Yariv Pinto[1,2], Nadrian C. Seeman[3], Karin Musier-Forsyth[2], T. Andrew Taton[2] and Richard A. Kiehl[1]; [1]Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota; [2]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota; [3]Department of Chemistry, New York University, New York, New York.

A method for manufacturing arrays of metallic nanowires with programmable spacing and nanometer-scale precision is needed for future electronic circuitry. We report the fabrication of Au nanowire arrays using a 2D DNA scaffolding as a growth template on a silicon substrate. Self-assembly by DNA scaffolding is a bottom-up approach for arranging nanometer-scale components with a theoretical precision of 0.34 nm, the separation between base pairs in a B-form, double-stranded DNA helix. This approach offers programmability in the arrangement of components through base sequence design. The 2D DNA scaffolding used in this study is constructed from a set of 21 synthetic oligonucleotides that are designed to assemble into four different double-crossover (DX) molecules, which in turn assemble into a 2D DNA crystal. The dimensions of the DX molecules are about 2 nm x 4 nm x 16 nm and the spacing between similar molecules in the 2D DNA crystal is 64 nm. One of the four DX molecules includes an extended single-stranded DNA feature that is designed to hybridize to oligonucleotides bound to nanoparticles functionalized with multiple strands of DNA. In the first step of the process, the DNA-functionalized Au nanoparticles are self-assembled into closely packed rows with precisely defined inter-row spacings by *insitu* hybridization to a preassembled 2D DNA scaffolding on a chemically treated SiO$_2$ surface on Si. Then, a selective catalytic enlargement process is used to link the Au particles, thereby forming a regular array of nanowires. Scanning electron microscopy (SEM) of the sample before catalytic enlargement confirms that rows of closely spaced metallic particles have been formed on the substrate, and SEM images after catalytic enlargement confirm the linking of the particles to form a regular array of Au nanowires with a spacing of ∼64 nm, the design value in the DNA template. This method for the fabrication nanowire arrays is broadly applicable to the manufacturing of nanoscale integrated circuits for logic, memory, sensing, and other applications.

11:30 AM AA4.8

1D, 2D and 3D Structures of Multicomponent Nanowires Assembled by Biological and Magnetic Interactions. Min Chen and Peter C. Searson; Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

The bottom up approach to device fabrication involves the synthesis and assembly of nanoscale building blocks. With advances in synthesis of nanoscale particles, there is increasing interest in assembly of diversely dimensional and symmetric structures through preferential interactions between nanoscale particles. With high affinity, Avidin-biotin technique has been widely used in immunology, histochemistry, affinity chromatography and other areas. Recently, Avidin-biotin technique has been exploited in self-assembly of nanoparticles. Here we report on the avidin-biotin directed assembly of multicomponent nanowires into one-dimensional chain, two-dimensional array and three-dimensional network. Magnetic and nonmagnetic nanowires with Au segments were fabricated by electrochemical template synthesis in anodized alumina template [1]. The Au segments were selectively functionalized with a biotin-terminated thiol [1]. One-dimensional nanowire chain was assembled by injecting avidin into biotin-terminated nanowires or by mixing avidin-terminated nanowires with biotin-terminated nanowires at 1:1 ratio. The results show that the average chain size depends on the avidin/biotin-terminated nanowire ratio, the reaction time, and the concentration of nanowires in the first experiment. Also, we studied the dynamic of mixing reaction by monitoring the growth of nanowire chain size. A model has been developed to explain the linearity relationship between average chain size and reaction time. Monte Carlo simulation of model agrees well with experiment results.

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 AA4.9

Molecular Templating of Layered Zirconium Phosphonates: Applications in Dental Restorative Composites. Benjamin Furman[1,3], Stephen T. Wellinghoff[2], Paul M. Thompson[2], Richard M. Laine[3] and H. Ralph Rawls[1]; [1]Restorative Dentistry, UT Health Science Center, San Antonio, Texas; [2]Materials Chemistry, Southwest Research Institute, San Antonio, Texas; [3]Materials 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 proven difficult to disperse homogeneously into organic resins. Organofunctional zirconium phosphonates offer an attractive alternative to equiaxed zirconia particles. The direct reaction of phosphonic acids with zirconyl chloride generally results in amorphous zirconium phosphonate structures. In this study, novel phosphonate precursors are shown to template the growth of ordered platy solids, analogous to functionalized nanoclay, in situ within a thermoplastic host polymer. These nanoplatelet fillers bear organic surface groups that interact favorably with a host polyester. 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 Kato[1], Masafumi Yoshio[1], Kenji Kishimoto[1], Hiroyuki Ohno[2] and Tomohiro Mukai[2]; [1]Department of Chemistry & Biotechnology, The University of Tokyo, Tokyo, Japan; [2]Department of Biotechnology, Tokyo University of Agriculture & Technology, Tokyo, Japan.

Self-organization processes of liquid crystals can be used to obtain anisotropic functional materials (1). Recently, we have reported that 2D or 1D ion-conductive materials have been prepared by macroscopically oriented smectic or columnar liquid crystals (2-4). These liquid crystals have block structures comprising of oligo(ethylene oxide)s or imidazolium moieties. Here we show these two series of nanostructured anisotropic ion-conductive materials. We focus on the preservation 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 monodomain in macroscopic scale are keys for the preparation of polymeric materials with enhanced anisotropic ion conductivities. (1) T. Kato, Science, 2002, 295, 2414-2418. (2) K. Kishimoto and T. Kato et al., J. Am. Chem. Soc., 2003, 125, 3196-3197. (3) M. Yoshio and T. Kato et al., Adv. Mater., 2002, 15, 351-354. (4) M. Yoshio and T. Kato et al., J. Am. Chem. Soc., 2004, 126, 994-995.

2:00 PM *AA5.2

Cooperative Dynamics in Multicomponent Supported Phospholipid Membranes. Atul N. Parikh, Annapoorna R. Sapuri-Butti, Chanel K. Yee, Sanhita S. Dixit and Alan W. Szmodis; Applied Science, UC Davis, Davis, California.

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/sphingomyelin 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 sphingomyelinase. 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 Shelnutt[1,2], Zhongchun Wang[3], Yujiang Song[1,3], Craig J Medforth[1] and Eulalia Pereira[4]; [1]Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; [2]Department of Chemistry, University of Georgia, Athens, Georgia; [3]Departments of Chemistry and Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; [4]CEQUP/Departamento de Quimica, Universidade do 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 biomimetic compounds (e.g., tetrapyrroles). Specifically, nanotubes and other nanostructures composed of porphyrins mimic the light-harvesting and photosynthesis functions of the chlorosomal rods and reaction centers of green sulfur bacteria. The porphyrin nanotubes 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 photoreduce aqueous metal salts to the zero-valent metals. The photosynthetic properties of the nanotubes composed of these photocatalytic porphyrins have been used to synthesize functional nanotube-metal composite sytems, which may lead to solar nanodevices that mimic photosynthesis to split water 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 nanomaterials. In micellar solutions, spherical metal nanodendrites 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. Synthetic control over the morphology of these nanoscale dendrites, sheets, and nanostructured 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 Ly 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 nanofeatures. 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 templates 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 for driving precursors into the small features and preferential assemble 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 Convection and Phase-Separation. Anna Balazs, Christopher Pooley and Olga

Kuksenok; Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

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, Tc, of the mixture. In particular, a binary AB fluid is confined between two plates in a gravitational field. The upper plate is fixed below Tc and hence, the nearby fluid phase-separates into A rich and B rich domains. The lower plate is fixed above Tc, and the surrounding fluid is in the 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 columns with convection, the periodic disturbance of these columns, and finally, chaotic dripping 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. Orlin 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 electric fields. 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 microseparation of the components and leads to the formation of layered particle crystal structures. Controlled on-chip assembly, drying, encapsulation and polymerization were used to make anisotropic "eyeball" and striped 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 contact 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 correctly-placed components. This approach offers 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. Ebeam lithography is used to pattern holes in resist on oxidized silicon substrates. A timed, isotropic wet etch converts the resist openings into near-hemispherical holes in the oxide. Different hole shapes are created by exposing larger and smaller regions of resist, which result in larger or smaller deviations from the ideal hemispherical hole shape. Templates and microspheres are coated with SAMs (ie. octadecyltrichlorosilane). The hydrophobic interaction between coated surfaces and the assembly fluid attracts components to the substrate. The assembly fluid is a mixture of acetone (~97%) and water (~3%); varying the mixture's composition varies the strength of the hydrophobic interaction between fluid and components. A megasonic transducer (1.7 MHz and about 10 W/cm2) was placed in a large water-filled beaker. A smaller beaker containing components, substrate, and assembly fluid was suspended in the large beaker, above the transducer. After a three minute assembly time, the substrate was removed from the fluid, and the number of particles assembled in the different-sized holes were counted. The results are quantified by assembly yield, the fraction of holes of a given size that are filled with particles. The assembly yield depends strongly on component-hole match (contact area). When the contact area is 5% of the total surface area of the particle, yield is 100%. From 0.8% to 2% contact area ratio, the assembly yield increases from 5% to 80%. This shows that templated assembly by selective removal is selective; optimization of fluid/surface interaction energy and megasonic transducer power may permit higher selectivities in the future. Models were created to examine the competing component retention and removal forces. The retention force reflects the change in free energy upon removing a component from a site, while the removal forces reflect the Stokes drag on the components from the acoustic streaming flow. The models show the high potential selectivity of this approach.

4:30 PM AA5.8
Obtaining Long-Range Order of Nanoscale Polymer Domains. Seth B. Darling[1], D. Sundrani[2] and S. J. Sibener[2]; [1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois; [2]The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois.

Fabrication of macroscopic domains of periodic nanoscale structures using self-organizing systems has attracted significant recent attention. Ultrathin diblock copolymer films, in particular, are promising candidates for bottom-up nanotemplates in hybrid organic-inorganic electronic, optical, and magnetic devices. These systems self-assemble into domains with a length scale tunable from ~10-100 nm; however, without further constraint, the domains have no preferred orientation and form a "fingerprint" structure. We present a new general method for defining an orientation and eliminating defects via the introduction of geometric anisotropy on silicon nitride 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. * D. Sundrani, S.B. Darling, S.J. Sibener, Nano Letters 4 (2004) 273-276; Langmuir 20 (2004) 5091-5099.

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

It is of 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 angels (0, 15, 30, 45 and 60 degree) and used secondary electron images to observe evolution of nanostructures 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 smoothening 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 Biomolecular Interactions at Self-Assembled Interfaces. Nicholas 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-laden 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 Reppy[1], Brad Pindzola[1], Stephen Hussey[1] and Anh Tram Nguuyen[1,2]; [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 discernable output 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 nano-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 polymer. Forming the coatings by filtration eliminates 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 neutral, 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 seen that the variation in 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 incorporated in these coatings by conjugation to the precursor diacetylene colloids and also by reaction with functional groups on the coating surface. We have used enzyme amplified immunoassays 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. Ian 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 novel, biomimetic system 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 electronically control the activation of 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 locally regulate 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 selective patterning of the electrode 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. Yunfeng Lu[1], Byron Mccaughey[1], Huisheng Peng[1], Xuan Li[1], Jiebin Pang[1], Xiang-Ling Ji[1] and C. Jeffrey Brinker[2]; [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 chameleons 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 amphiphilies and their self-assembly and polymerization to form a new class of adaptive materials that exhibit reversible order-disorder and chromatic transitions in response to thermal or chemical stimulation. Such dynamic assembly provides systems with responsive, adaptive and self-healing functionality analog 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 its 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 highights 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 oriented 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 Gin[1,2], Weiqiang Gu[1], Yanjie Xu[2], Cory Pecinovsky[1] and Jizhu Jin[1,2]; [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 "analogs" to zeolites and mesoporous sieves can be synthesized by cross-linking lyotropic liquid crystals (LLCs) containing reactive headgroups in nanoporous mesophases. 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 order. 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 successfully bring 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 general means of incorporating wide range of functional groups into LLC phases. We have found that even monomers containing large chiral catalytic groups and controlled radical polymerization catalysts can be "templated" into LLC phases through the use of these structure-directing agents. This talk will present the synthesis of these templated materials and their catalytic performance.

11:00 AM AA6.7
Fabrication of Novel Types of Colloidosome and Liposome with Gelled Cores For Drug Delivery Applications. Vesselin N. Paunov[1], Paul F. Noble[1], Olivier J. Cayre[1], Rossitza Alargova[2] and Orlin D. Velev[2]; [1]Department of Chemistry, University of Hull, Hull, North Humberside, United Kingdom; [2]Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

Colloidosomes and liposomes are core-shell structures that consist of an aqueous core and a shell formed by fused colloidal particles or lipid bilayers. Recently, it has been recognised that such microcapsules offer a great potential in controlling the permeability of entrapped species in pharmaceutical, cosmetic and food products. Here we report a versatile fabrication method of novel colloidosomes microcapsules which is based on the following 3 stages: (i) Hot aqueous solution of gelling hydrocolloid is emulsified in a suitable oil in the presence of solid polymer particles dispersed in the aqueous phase to produce a water-in-oil emulsion stabilised by the solid particles and the system is cooled off to set the gel. (ii) The produced suspension of aqueous gel microcapsules coated with a particle monolayer is separated by filtration to remove the oil phase. (iii) The microcapsules are washed and collected into water. This methodology allows us to produce colloidosome microcapsules of diameters varying between several tens of micrometers to several hundreds of micrometers. The function of the gel cores was to support the particle shell around them and to give the microcapsules enough stiffness to be separated from the oil phase by filtration. Following this technique we have been able produce three different types of colloidosome microcapsules. (a) By combining monodisperse amino-latex microparticles and an oil which swells the latex we have fabricated integral colloidosomes of porous membrane where the pore size is controlled by the degree of swelling. (b) By using monodisperse amino-latex particles and cross-linking agent we were successful in producing colloidosomes of spherical particle monolayers, where the membrane pores are defined by the particle size. (c) By using polymer micro-rod particles as emulsifiers we have synthesized for the first time 'hairy' colloidosomes which shells consists of randomly assembled rod-like particles. We also report the fabrication of novel hybrid giant liposomes with cores of an aqueous gel based on an extension of the Pautot technique. It involves the following three steps: (i) A lipid-stabilised water-in-oil emulsion is prepared in the presence of a gelling hydrocolloid in the aqueous phase. (ii) The water drops, coated with a lipid monolayer are gelled at lower temperature to produce gel beads. (iii) The gelled beads are transferred from the oil phase through the planar oil-water interface where they pick up a second lipid monolayer and convert into giant liposomes of gelled aqueous cores. We maintain a saturated lipid monolayer at the planar oil-water interface by injecting lipid solution in a spreading solvent. These novel microcapsules have higher stability and mechanical strength than conventional liposomes and may find applications as drug delivery vehicles and for controlled release of proteins, vacines, cosmetic and food supplements.

11:15 AM AA6.8
Scattering and Energy Level Splitting in Dynamic Nanoscale Core/ Shell Systems. David Sebba and Anne A. Lazarides; Dept of Mech Eng and Mat Sci, Duke University, Durham, North Carolina.

The plasmon resonances of dynamic DNA-linked gold nanoparticle assemblies are investigated. The linked assemblies reversibly expand and contract in the absence and presence of complementary strand driven DNA duplex formation. The two state system displays state-dependent scattering properties and resonance levels, with strong scattering and energy level splitting in the contracted state. Implications for ultrasensitive DNA detection are discussed.

11:30 AM AA6.9
Responsive Supramolecular Particles from Assemblies of Homopolymers. Huisheng Peng and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Polymeric nanometer- or micrometer- sized objects, in particularly, polymeric hollow spheres, are of great interest for controlled delivery, cell mimics, biosensors, and other applications. The most studied synthesis procedures often involve the formatioom of micelles from block copolymers in the selective solvents, cross-linking of the micellar corona, and the removal of the core by chemical degradation. However, this approach is limited by the difficulties of synthesizing the block copolymers containing both cross-linkable and degradable blocks. Here we demonstrate the formation of responsive polymeric micelles in water hydrogen bonding of two homopolymers, polysulfonated aromatic poly (ether ether ketones) (PEK) and poly (allylamine) (PAA). Such supramolecular assemblies demonstrate reversible association and disassociation at different pHs, providing a low-cost and efficient route towards hollowed polymeric spheres. Model drug molecules can be readily incorporated into the supramolecular carriers and released at controlled conditions, indicating a great potential for drug delivery. The control of assembly and function exhibited in the system is a significant progress towards the synthesis of the advanced materials.

11:45 AM AA6.10
Detection of Biomolecules from MBE-Grown II-VI Quantum Dots by Means of SERS Spectroscopy. Lucia G. Quagliano[1], R. Livingstone[2], M. Munox[2], N. Perez[2], M. C. Tamargo[2] and J. R. Lombardi[2]; [1]Institute for Nanostructured Materials, Consiglio Nazionale delle Ricerche, Roma, Italy; [2]Department of Chemistry, The City College of New York, New York, New York.

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 (1), 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 small Raman cross section, which results in a very 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 spectroscopy is a very sensitive technique that employs rough substrates with structures in the nanometer range to enhance the Raman signal produced by adsorbed species. In SERS the effective Raman cross-section can be increased by many orders of magnitude, while simultaneously suppressing fluorescence. We observed the SERS spectra of tyrosine, adenine, and tryptophan molecules adsorbed at a very low concentration on self-assembled CdSe/CdZnSeMg quantum dots. These spectra provide detailed molecular information on composition, structure, and orientation. This study shows that 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 semiconductor quantum dots as the sensing probe are a very attractive area. (1) Lucia G. Quagliano, J. Am. Chem. Soc. 126 (2004) 7393

SESSION AA7: Nanoarrays and Tunable Optics
Chair: Andrew Dattelbaum
Thursday Afternoon, March 31, 2005
Room 3011 (Moscone West)

1:30 PM *AA7.1
Some Recent Developments in Colloidal Self-Assembly. Younan Xia, Chemistry, University of Washington, Seattle, Washington.

A range of new developments related to the synthesis and self-assembly of colloidal building blocks will be presented in this talk. For synthesis, I will discuss new strategies that have been developed for preparing monodispersed spherical colloids from materials with high refractive indices. Typial examples include titania, amorphous selenium, chalcogenides, and metals with relatively low melting points. The surfaces of these spherical colloids can be further coated with conformal shells to tune their interactions and optical properties. Their interiors can also be loaded with iron oxide nanoparticles to give them superparamagnetism. Similar to spherical colloids made of silica or polystyrene, these spherical colloids can be readily assembled into crystalline lattices to be used as photonic crystals. They can also be organized into discrete clusters with well-controlled shapes and structures. The talk will be concluded with a brief discussion on the potential applications of these self-assembled structuers of colloidal particles.

2:00 PM AA7.2
Controlled Deposition and Modification of Conductive and Antireflective Nanoparticle Coatings. Brian G. Prevo, Yeon Hwang, Joseph C. Fuller and Orlin D. Velev; Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina.

The convective assembly method for particle deposition was originally designed for rapid assembly of photonic crystals from monodisperse particles. However, we will demonstrate that the method allows facile fabrication of nanoparticle coatings with a range of other useful properties. Two types of nanocoatings that will be presented are conductive metallic films from metal nanoparticles, and antireflective (AR) films from silica microspheres. Uniform nanocoatings were deposited in minutes directly from aqueous suspensions by convective assembly at high volume fraction. 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, a rapid post-deposition annealing 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-percolated nanoparticle structure to a discontinuous insular structure. The surface plasmon resonance peak could be tuned by heating to any value from 800 nm to 565 nm. The control over film structure and thickness via convective assembly also provides 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 with porous or composite films. In a single step, the 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 macroscopic optical properties imparted by the silica nanocoatings.

2:15 PM AA7.3
Large-scale Fabrication of Ordered TiO_2 Nano-Bowl Arrays. 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 fabrication of 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 TiO_2 nano-bowl arrays. The process starts with a self-assembled monolayer of polystyrene spheres, which was used as the template for atomic layer deposition of TiO_2. The top half of the TiO_2 coated PS spheres were then removed with an ion milling machine. In the final step, the PS hemispheres left on the substrate were etched away by toluene, resulting in a highly-ordered array of TiO_2 nano-bowls. Annealing at 850°C for 2 hours transformed the amorphous film into polycrystalline anatase TiO_2. SEM studies showed that the periodic structure of the PS monolayer was well preserved during the entire process. The TiO_2 walls are $\sim$25 nm in thickness and no distortion was observed after the PS hemispheres were removed. The nano-bowls exhibit smooth interior and exterior surfaces and uniform size and thickness, which were not changed after the annealing process. TEM studies confirmed their anatase phase and showed that the TiO_2 bowls have a polycrystalline structure with a fairly large grain size, typically $\sim$50 nm. As one of the important functional semiconductors, TiO_2 exhibits promising applications in solar cell, photocatalytic, photonic crystal and photovoltaic technology. The robust and highly-ordered anatase TiO_2 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 this 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 for bio species, such as cells, if the interior surface is coated with 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 and Nano-Optoelectronics. Y. F. Mei[1], G. G. Siu[1], Ricky K. Y. Fu[1], Paul K. Chu[1], Z. M. Li[2] and Z. K. Tang[2]; [1]Physics & Materials Science, City University of Hong Kong, Kowloon, Hong Kong; [2]Physics, 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 Martin et al. The self-organization 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 fabricated on porous anodic alumina (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 mechanism. Two applications of the nanoscale islands are presented. A novel nano-MOS array: metallic carbon nanotube connected with nanoscale SiO2 island inside insulated alumina nanochannel based on silicon substrate was fabricated via a Si-based PAA template. The electrical properties were determined by I-V and C-V measurements. The lower work function of the multiwalled CNTs induces lower flat-band voltages (VFB) compared to the conventional behavior of MOS. This structure is important for CNTs and PAA template via the self-assembled 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 Cu2O. 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 Cu2O is due to the alkalinity of the anodized solution. However, the oscillations of the potential 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 Cu2O because of quantum confinement effects.

2:45 PM AA7.5
Conjugated Oligomer Self-assembly: Correlation between Molecular Architecture, Microscopic Morphology and Optical Properties. Mathieu Surin[1], Philippe Leclere[1], Prashant Sonar[2], Andrew C. Grimsdale[2], Klaus Muellen[2], Steven De Feyter[3] and Roberto Lazzaroni[1]; [1]Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; [2]Max Planck Institute for Polymer Research, Mainz, Germany; [3]Laboratory 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 facile substitution.[1] Understanding and exploiting the relationships between morphology and optoelectronic 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 microscopic morphologies of 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 pi-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 light-emitting applications.[2] The microscopic morphology of various co-oligomers of fluorene with thiophene is also investigated. Due to their improved stability (compared to commonly used oligo- and polythiophene), these compounds are particularly interesting for field-effect transistor (FET) devices with high FETs performances.[3] We show that various types of nanostructures can be obtained, due to 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 delimited by the stamp features.[4] References [1] Neher, D. Macromol. Rapid Commun. 22 (2001), 1365. ; Scherf, U.; List, E. W. J. Adv. Mater. 14 (2002), 477. [2] Surin, M. et al. Chem. Mater. 16 (2004), 994. [3] Sirringhaus, H. et al. Science 290 (2000), 2123 ; Meng, H. et al. Chem. Mater. 15 (2003), 1778. [4] Cavallini, M.; Biscarini, F. Nanoletters 3 (2003), 1269.

3:30 PM *AA7.6

Photonic Switches Based on Photo-Optic Periodic Nanostructures. Timothy J. Bunning[1], Augustine Urbas[3], L. V. Natarajan[2], V. P. Tondiglia[2] and R. L. Sutherland[2]; [1]Air Force Research Laboratory, WPAFB, Ohio; [2]SAIC, Dayton, Ohio; [3]Anteon Corp., Dayton, Ohio.

Spatially periodic, two-phase nanocomposites with appreciable refractive index variation leads to the formation of a variety of diffractive transmissive and reflective gratings with application in a number of photonic applications. The ability to modulate this spatially periodic refractive index profile enables a number of tunable or switchable photonic applications. We report here on the fabrication of multi-dimensional structures whose optically properties can be modulated by spectrally selective light. The incorporation of photochromic-based liquid crystals into periodically spaced nanoscale LC droplets leads to optically transparent structures that exhibit Bragg diffraction properties. Upon illumination with a particular wavelength of light, an isothermal phase change can be induced which modulates the refractive index profile. Control of the two-phase morphology is key to optimizing 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.

4:00 PM AA7.7

Size-dependent Optical Properties of Vanadium Dioxide Nanoparticle Arrays. Rene Lopez, Richard F. Haglund and Leonard C. Feldman; Physics and Astronomy, Vanderbilt University, Nashville, Tennessee.

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 VO_2. In contrast to previous VO_2 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 state during the evolving phase transition. The effects appear to arise because of the underlying mesoscale properties of VO_2, the heterogeneous nucleation underlying the phase transition and the incoherent coupling between the nanoparticles undergoing an order-disorder-order transition. VO_2 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 VO_2.

4:15 PM AA7.8

Langmuir-Blodgett Technique in the Fabrication and Synthesis of Nanostructured Materials. Hong Yang[1,2], Xiaowei Teng[1] and Qijie Guo[1]; [1]Dept of Chemical Engineering, University of Rochester, Rochester, New York; [2]Laboratory 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, I will present our recent work on the development on 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 also been 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 (PXRD), energy disperse 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).

4:30 PM AA7.9

Ferroelectric Three-Dimensionally Ordered Macroporous Thin Films. Catherine Barron[1], Martyn McLachlan[1], Qi Zhang[2], Roger W. Whatmore[2] and David W. McComb[1]; [1]Materials, Imperial College London, London, United Kingdom; [2]Advanced Materials, Cranfield University, Cranfield, United Kingdom.

Recent results on the synthesis, characterisation and investigation of electro-optical properties of ferroelectric three-dimensionally ordered macroporous for potential use as a tunable photonic crystal will be reported. The potential technological applications of a photonic crystal with a tunable photonic band gap are extensive, not least because tuning of the band gap could be used for on/off switching of the transmitted wavelengths. While the challenge of obtaining a complete PBG in all crystallographic directions in colloidal photonic crystals is considerable, full PBG behaviour is not a crucial requirement for a tunable photonic crystal to be useful. In order to use chemistry to tune the stop-band in photonic crystals we have utilised template-directed synthesis routes to form ferroelectric three-dimensionally ordered macroporous thin films. The structure and properties of the thin films produced using sol-gel precursors for the ferroelectric perovskites, Pb(ZrxTi1-x)O3 (PZT) and La-doped PZT, and thin film colloidal crystals templates will be reported.

4:45 PM AA7.10

Spontaneous Polarization-induced Asymmetric Growth of Cadmium Selenide Nanobelts. Christopher Ma, Georgia Institute of Technology, Atlanta, Georgia.

Wurtzite structured Cadmium Selenide (CdSe) is an important II-VI semiconducting compound for optoelectronics. CdSe quantum dots are the most extensively studied quantum nanostructure due the size tunable properties, and they have been used as a model system for investigating a wide range of nano-scales electronic, optical, optoelectronic, and chemical processes. CdSe was also the 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 pillars 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 nanobelt 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 (SPA) growth. The growth can cause fingers to grow from the sides. These polar nanobelts have applications ranging from piezoelectric cantilevers to bio-sensor arrays. [1] Chris Ma, Yong Ding, Daniel Moore, Xudong Wang and Z.L. Wang* "Single-Crystal CdSe Nanosaws", 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 Dickon 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^{o}C and 1060^{o}C for an hour under a pressure of $\sim$10 Torr. The morphology and microstructure of the nanobelts were characterized by x-ray diffractometry and electron microscopy, respectively. The CdS nanobelts prepared at 840^{o}C had a thickness of about 100 nm. Their length ranged from 20 to 80 mm, and width varied from 100 nm at the tip to 2 mm near the bottom. As the sintering temperature increased, the dimension of these belts increased. We also found that these nanobelts grew towards the direction. During the growth of the nanobelts, CdS vapor dissolved into the Au droplet and precipitated at the liquid/solid interface upon supersaturation. Two types of 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 nanobelt grew out from the catalytic droplet when the Au particle was too large to be 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 temperature exhibited two peaks. One peak was found at $\sim$510 nm, and the other between $\sim$706 and $\sim$756 nm. The first peak corresponded to the intrinsic emission of CdS, while the second one corresponded to the sulfur defects 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 was increased from 880 to 1040^{o}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 160^{o}C. It was possible that the sulfur vacancies in the CdS samples sintered at different temperatures 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 on the effect of sintering temperature on their optical properties will also be presented.

AA8.2

Novel Fabrication of Functional Imprinting Patterns; Molecularly Imprinted Polymer (MIP) with Specific Molecular Recognition Function. Kyung M. Choi[1,2] and Kenneth J. Shea[1]; [1]Department of Chemistry, University of California-Irvine, Irvine, California; [2]Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Microfabrication technology offers us rapid assembly and integration of small features fabricated on a variety of substrates to produce numerous active devices. Especially, plastic/organic/molecular electronics produce economic devices with high performance using 'soft' materials. Due to our increasing demands in miniaturization, recently, there is an ongoing search for the pattern integration using functional materials to fabricate patterns with specific functions. For example, we present here an unconventional approach to the 3-D microfabrication of functional polymers with specific molecular recognition function to expand current patterning technology to advanced levels. We introduced a molecularly imprinted polymer (MIP) as a promising candidate of the patterning tasks. MIP is a highly cross-linked macroporous thermoset with both high internal surface areas and specific molecular recognition sites, which may be useful for chemical or bio detective technology. Using the MIPs' system attached with fluorescence template molecules, we fabricated a 3-D molecular architecture by 'microstereo-lithography' and generated fluorescence MIP patterns using 'microfluidic photomasks'. We also synthesized nano- or micro-sized MIPs polymer particles using a 'microfluidic droplet reactor' to obtain 'monoclonal' MIPs particles with only high affinity receptor sites to achieve high performance molecular recognition function.

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 Viville[1], Michel Schappacher[2], Alain Deffieux[2], Redouane Borsali[2], Julien Bernard[2] and Roberto Lazzaroni[1]; [1]Chemistry of Novel Materials, University of Mons-Hainaut, Mons, Belgium; [2]Laboratory of Chemistry of Organic Polymers, University of Bordeaux, Pessac, France.

In this work, comb-like and arborescent polystyrene-based grafted copolymers are studied. These copolymers are synthesized by the graft-on-graft technique consisting in the iterative grafting of end-functional polystyryl lithium chains onto reactive poly(chloroethyl vinyl) ether (PCEVE) backbones. The method allows for the preparation of quasi-perfect (PCEVE-g-PS) comb-like molecular architectures. In addition, the architectural complexity of these molecules can be significantly increased from a zero-generation comb-like (PCEVE-g-PS) grafted copolymer to a first-generation hyperbranched (PCEVE-g-(PS-b-(PCEVE-g-PS))) copolymer bearing arborescent lateral branches. The method is thus a versatile way to control the dimensionality of single molecules. Tuning the degree of polymerization of the constituting PCEVE and PS sequences of the grafted copolymers allows one to prepare a large variety of molecular dimensions from thin (short or elongated) cylinders to much thicker rod-like objects and perfect spheres. The morphology of the obtained molecules and their organization on surfaces is investigated by Tapping mode Atomic Force Microscopy (TMAFM). 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 in order to prepare new water-soluble 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 deprotection of the hydroxyl functions of the vinyl ether units then yields a dendrigraft 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 deprotection step are investigated in solution using light scattering (elastic SLS and quasi-elastic DLS) and as isolated unimolecular deposits using atomic force microscopy and cryomicroscopy. The obtained results using both imaging techniques are in agreement with those obtained by SLS and DLS and provide additional information on the internal 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 dendrigraft branches and associate with neighboring blocks to form separate phases.

AA8.4

Transferred to AA4.9

AA8.5

Nanometer Scale Patterning using Di-Block Copolymer. Zuoming Zhao, Tae-Sik Yoon, Wen Feng, Biyun Li and Ya-Hong Xie; Materials Science and Engineering, UCLA, Los Angeles, California.

Di-block copolymer thin films of PS-PI, PS-PB and PS-PMMA are investigated on Si substrates. The morphology evolution with polymer thickness is studied using optical microscopy. As-coated polymer films exhibit a very smooth surface. After annealing polymer over glass-transition temperature, the polymer exhibits a smooth surface only at certain thickness L_0. Transmission electron microscopy is used to study the microphase separation in polymer at different stages. Clear phase separation is observed in the polymer after staining with osmium tetraoxide (OsO_4). Long time annealing increases the long-range ordering. After treatment with ozone, disappearance of dark dots due to staining of osmium and appearance of white hole indicate that the polymer with double-bond is removed from copolymer film. Scanning electron microscopy shows that polymer films after reactive ion etching give a regular hole pattern which can serve as mask for nanometer scale patterning.

AA8.6

Magnetic Behaviors of Hydrated Cobalt Oxide Sheets Separately Intercalated in the Gallery of Mica. Kiyoshi Fuda and Jun-ichi Shimoyama; Research Institute of Materials and Resources, Akita University, Akita, Japan.

Exfoliation of layered materials often leads to remarkable modifications in the properties of the mother body. Sodium Cobalt oxide system, NaxCoO2, is an interesting example, because it gives a transformation from normal conductor to superconductor phase via intercalation of bilayer of water molecules between the CoO2 sheets. We have reported that monolayer of such hydrated CoO2 sheet can be formed separately in the gallery of mica by means of combination of intercalation and soft chemical technique. Here we studied the magnetic behaviors of the CoO2 / mica layered nanocomposites to extract the effect of the special separation of the CoO2 sheets on the properties of the spin system. From the study of the temperature dependence and field dependence of the magnetization, we found an anomalous hysteresis in the M-H behavior at 50K as well as in the M-T one below this temperature. The magnetization grows non-linearly with repeated scans of the magnetic field at 50K. Below this temperature, an apparent discrepancy between the field-cooled (FC) magnetization and the zero-field-cooled (ZFC) one was also found. On the other hand a magnetization independent of temperature was found in the region, 100K<T<300K, indicating a Pauli paramagnetism. The anomalous behaviors appeared in our system will be discussed comparing with the other layered CoO2 systems.

AA8.7

Lipid Membrane Supported on a Nanoscale Structured Silicon. Andrea L. Slade[1], Julie A. Last[1], Reema R. Zeineldin[2], Paul Bisong[3], Michael J. O'Brien[3], Linnea K. Ista[2], Steven R. J. Brueck[3], Gabriel P. Lopez[2] and Darryl Sasaki[1]; [1]Biomolecular Materials and Interfaces, Sandia National Laboratories, Albuquerque, New Mexico; [2]Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; [3]Center for High Technology Materials, University of New Mexico, Albuquerque, New Mexico.

A unique composite nanoscale architecture that combines the molecular dynamics of lipid membranes with a corrugated nanotextured silicon wafer was prepared and characterized via 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 successfully fused with a phospholipid 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 lipids exhibited anisotropic mobility coincident with the silicon substructure. These results show that while the lipid membrane maintains much of its self-assembled structure in the composite architecture, the silicon substructure indeed 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.

AA8.8

Studies of Single-Molecule Nanostructures Formed by Polyquinoline Bottlebrushes. Jessica Maryn Hancock[1], Yan Zhu[1], Maksudul M. Alam[2] and Samson A. Jenekhe[2,1]; [1]Chemistry, University of Washington, Seattle, Washington; [2]Chemical Engineering, University of Washington, Seattle, Washington.

Polymer bottlebrushes, 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 polymer bottlebrushes, such as polystyrene side chains with poly(methyl methacrylate) main chains, have been visualized as beautiful worm-like cylindrical nanostructures. To marry features of bottlebrush molecules and conjugated polymers, our group recently synthesized a series of conjugated polymer bottlebrushes consisting of polystyrene backbones of varying chain lengths with polyphenylquinoline pendant side chains of varying chain lengths. The nanostructural, photophysical and electroluminescent properties of this series of bottlebrushes are reported here. Atomic force microscope and scanning electron microscope 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 bottlebrushes showed enhanced electroluminescence efficiency compared to identical devices made from the corresponding polyquinoline homopolymer. Our results show that bottlebrush polyquinolines form single-molecule nanostructures with enhanced electronic and optical properties.

AA8.9

One Step Preparation of Hollow Gold Spheres. Peter K. Stoimenov, Galen D. Stucky and Timothy J. Deming; Chemistry, University of California at Santa Barabra, 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 as 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 ?m 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 shown that the hollow metal spheres are very smooth and are not consisting of loosely bound nanoparticles but as a single continuous metal shell.

AA8.10

Biotemplate Directed Growth of Metallic Nanowires. Autumn Carlsen[1], Narender Rana[1], Silvana Ngo[2], Christopher Kossow[1], Seiichiro Higashiya[2], Natalya Topilina[2], Yu Zhu[1], Vladimir Ermolenkov[2], Christopher Wells[2], James Raynolds[1], Kathleen Dunn[1], Eric T. Eisenbraun[1], Igor Lednev[2], Robert E. Geer[1], John T. Welch[2] and Alain E. Kaloyeros[1]; [1]College of Nanoscale Science and Engineering, University at Albany, State University of New York, Albany, New York; [2]Department of Chemistry, University at Albany, State University of New York, Albany, New York.

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 [(GA)3GY(GA)3GE(GA)3GH(GA)3GK where G=glycine, A=alanine, Y=tyrosine, E=glutamic acid, H=histidine, and K=lysine] folding in a β-sheet.(1) Results are presented herein from the successful demonstration of the attachment of commercially available monomaleimido gold nanoparticles to functionalities on the modified polypeptide. Transmission electron microscopy analysis revealed an average capped-nanoparticle diameter of 1.4 nm. Repetitive coding DNA sequences designed to produce the polypeptide were formed through unidirectional oligomerization of the monomer and oligomerized units. To enable cloning into recipient plasmids, the prepared units were subjected to ligation from head-to-tail in the presence of adaptors. Known biochemical methods were employed to amplify these units. After cloning in expression vectors, the DNA sequences were expressed in E. coli hosts. Ni-NTA columns were used to purify the polypeptide, once the cells had been collected and lysed. Two complementary treatments were then employed for gold particle attachment to polypeptide templates. The first treatment involved the use of non-functionalized peptides. The second treatment followed the approach reported by Gregori et al.,(2) the polypeptide was functionalized with cysteine residues for the purpose of gold labeling with the monomaleimido gold nanoparticles. Atomic force microscopy was then performed on both graphite and nickel substrates that had been exposed to aqueous solution containing the two types of polypeptide systems. The polypeptides appeared to form long fibrils. Scanning electron microscopy imaging was subsequently performed on a nickel substrates that had been exposed to aqueous solution containing both gold nanoparticles and polypeptide. Resulting investigations indicated the successful ionic-based directed attachment of gold to non-functionalized peptides. Findings from these investigations will be reported, along with similar studies of potential gold nanoparticle attachment to treated peptides. Support from the following is gratefully acknowledged: Microelectronics Advanced Research Corporation (MARCO), the Defense Advanced Research Projects Agency (DARPA), and the New York State Office for Science, Technology, and Academic Research (NYSTAR) through the National Focus Center Program. REFERENCES (1) Higashiya, S.; Ngo, S.; Bousman, K.; Welch, J.; Rana, N.; Carlsen, A.; Eisenbraun, E.; Geer, R.; Kaloyeros, A. Polym. Mat. Sci. Engin. 2003, 89, 466. (2) Gregori, L.; Hainfeld, J.; Simon, M.; Goldgaber, D. J. Biol. Chem. 1997, 272, 58.

AA8.11

Fabrication and Characterization of Epitaxial $BiFeO_3$-$BaTiO_3$ Nanoscale Hybrids using Nanosphere Lithography. Ram S. Katiyar, Rajasekarakumar Vadapoo and Sudipta Bhattacharyya; 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 opportunities for potential applications in information storage, the emerging field of spintronics, and sensors. Recent years 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 basic understanding of the underlying mechanisms of ferroelectricity 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 coupling 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 $SrRuO_3$ 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 form 50 −100 nm were deposited on these porous templates layers 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 obtained from 300 − 400 nm diameter PS templates were having the lateral dimension of 80 −100 nm as observed from SEM and AFM measurements. The $BiFeO_3$ −$BaTiO_3$ nano−islands were post annealed in oxygen at 650 ^{o} C for 1 h. X−ray diffraction studies showed the formation of crystalline and epitaxial BFO−BT on both $SrTiO_3$ and on $SrRuO_3/SrTiO_3$ heterostructures. The characterization of individual nano-structure on conducting substrates with piezo −force microscopy will be presented in this report. The feasibility to produce nanostructures with less than 50 nm lateral sizes have been verified in laser ablated Pt using PS diameter of 100–200 nm. Fabrication of similar structures with $BiFeO_3$ –$BaTiO_3$ was found to depend on the thickness of the film and the choice of the substrates. Systematic studies on obtaining ordered arrays with sub 50 nm lateral dimensions over a wider range of substrates and thickness is underway.

AA8.12

Patterning Colloidal Crystals in Two-Dimensionally Addressable Microfluidic Networks. Jau-Ye Hsu, Chun-Wen Kuo and Peilin Chen; Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan.

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 issues 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-assembly to assemble building blocks such as colloids, nanotubes and 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 formation of the self-assembled 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 to form 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 conducting combinatorial researches in the microfluidic networks. 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. Xiaowei Teng[1] and Hong Yang[2]; [1]Chemical Engineering, University of Rochester, Rochester, New York; [2]Department 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 the properties. A face-centered tetragonal phased FePt-containing inorganic nanocomposite has been made from Pt@Fe2O3 core-shell nanoparticle precursors under H2/Ar atmosphere at the enhanced temperatures. After annealing, multi-component magnetic nanocomposites was observed. X-ray diffraction and ultrahigh vacuum-canning transmission electron microscopy (UHV-STEM) data showed fct FePt phase in the annealed core region and fine edge electron-energy-loss spectroscopy (EELS) analysis showed the existence of iron 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, Jeong-Ho Park, Chae-min Chun and Dong-Yu Kim; Department of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 1 Oryoung-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 the complete and wide photonic band gap. 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 in self-assembled silica colloidal crystals. Macroporous 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 the light, azobenzene chromophores performed photoisomerization and orientational redistribution. Photo-orientation of azo chromophores caused the refractive 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.

AA8.15

Concentric Ring Formation in a Self-Organizing Metallic System. Vandana Panwar and Prasenjit Sen; School of Physical Sciences, Jawaharlal Nehru University, Delhi, Delhi, India.

Being a universal phenomenon, pattern formation continues to draw widespread attention encompassing biological, chemical, hydrodynamical and nonlinear optical systems. Situations where patterns have been seen in metals are limited to ion irradiation and sputtered surfaces [1], dendritic growth [2] and electrochemical dissolution [3]. Circular ring patterns have never been observed in a metal. As nonlinearities introduced in a dynamical system are known to induce spatial patterns, we employ electro-explosion of wires in a modified Z-pinch system in the needle-plate configuration to introduce nonlinearities in a metal. For iron and tungsten needles exploding on an iron plate, we find evidence of pattern formation of clear concentric rings frozen in the metal plate. Single wire, single explosion (SWSE) experiments were carried out in a specially designed reactor vessel using an iron plate polished to a roughness of the order of 50-500 nm as one of the electrode with micron sized iron and tungsten tips prepared by electrochemical etching as another electrode. A special arrangement is used to bring the tip close to the stationary plate in a controlled fashion. The explosions were carried out in water medium at 48 V DC. The current through the needle-plate geometry is recorded with a digital oscilloscope with a base time resolution of 2.5 ns. We establish electro-explosion by monitoring time evolution of the current showing heating, melting, explosion, i.e., evaporation of wire and then restrike or reignition after a certain dwell time. The exploding needle-plate system brings the plate instantaneously to its melting point, generating shock waves which travel through the melt. The shock waves transform the melt into micron-sized particles as confirmed by our AFM measurements. The ring patterns are a result of stationary waves set up in the melt, emanating naturally with cylindrical symmetry from the center of the melt, which resembles now a vibrating liquid surface. As this process takes place far away from equilibrium, the configuration gets frozen in the plate. The needle-plate geometry employed mimics a circular domain. We observe that this symmetrical state (concentric rings) is not trivial, as altered voltage conditions between the needle and plate, forces this self organizing system to lose stability to a state with less symmetry. References: [1] Eric Chason and Michael J. Aziz , Scripta Materialia 49, 953 (2003). [2] R. Trivedi, Shan Liu, and S. Williams, Nature Materials 1, 157 (2002). [3] Nils I. Jaeger, Ralph D. Otterstedt, Adrian Birzu, Brian J. Green, and John L. Hudson, Chaos 12, 231 (2002).

AA8.16

In Situ TEM Study of Self-Organization Process of Three-Dimensional Void Superlattice Formation in Electron Irradiated CaF_2. Tianhua Ding[1], Sha Zhu[1] and Lumin Wang[2]; [1]Department of Nuclear Engineering and Radiological Science, Univ. of Michigan, Ann Arbor, Michigan; [2]Department of Material Science and Engineering, Univ. of Michigan, Ann Arbor, Michigan.

CaF_2 is widely adopted as deep-UV window material and thin film optical coating. It has been known that ordered defect superlattices may form in electron irradiated CaF_2. However, the nature of the defects on the superlattice point (i.e., Ca colloids or voids) has not been certain and the self-organization mechanism has not been fully understood. In this study, both natural and synthetic CaF_2 were irradiated under 200 keV electron beam with in situ TEM observation of the dynamic process of defect ordering. Through-focus bright field images from three zone axes (100), (110) and (111) demonstrated that the superlattice structure is simple cubic. Energy-filtered transmission electron microscopy (EFTEM), high-angle annular dark-field (HAADF) STEM imaging, as well as thickness mapping, were used to characterize the void nature of the superlattice formed under electron irradiation. The superlattice reached steady state after an electron dose of $6\times10^{20}e^-/cm^2$ with void radius about 5-6 nm. Videos recorded during the in-situ observation reveal the dynamic self-organization process of the void superlattice. Coalescence was prevalent at the initial stages. Migration and preferential growth were dominant at the final stages of the superlattice formation. At a dose higher than $1\times10^{21}e^-/cm^2$ the superlattice structure was destroyed. These critical doses of void 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.

AA8.17

Photoinitiator System for Visible Wavelength Laser Writing of Thiol-ene H-PDLC Bragg Gratings. Dean P. Brown[1,2], Lalgudi V. Natarajan[3], Vincent P. Tondiglia[3], Richard L. Sutherland[3], Rachel Jakubiak[1], Richard A. Vaia[1] and Timothy J. Bunning[1]; [1]Air Force Research Laboratory, Materials & Manufacturing Directorate, WPAFB, WPAFB, Ohio; [2]SOCHE, Dayton, Ohio; [3]SAIC, Dayton, Ohio.

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 which minimizes the available periodicities 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 near 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, through the use of 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 photoinitiator further. 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 of the gratings was 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. Jennifer Lynn Pincus[1], Menake Piyasena[2], Gabriel P. Lopez[2] and Darryl Y. Sasaki[1]; [1]Biomolecular Materials and Interfaces, Sandia National Laboratories, Albuquerque, New Mexico; [2]Chemical Engineering Department, The University of New Mexico, Albuquerque, New Mexico.

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 membrane 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 yet biocompatible and rapidly responsive to aqueous phase analytes. 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.

AA8.19

Morphological Development at the Interface of Polymer/Polymer Bilayer with in-situ Compatibilizer under Electric Field. Dong Han Kho[1], Seung Hun Chae[1], Unyong Jeong[2], Hwang Yong Kim[1] and Jin Kon Kim[1]; [1]Chemical Engineering, Pohang University of Science and Technology, Pohang, Gyungbuk, South Korea; [2]Chemistry, University of Washington, Seattle, Washington.

In this study, electric field was applied to reactive bilayer thin films consisting of poly(methyl methacrylates-ran-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 (λmax) 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-g-PS. The morphology of the pillars was influenced specially by the roughness from the shape of copolymer formed in the interface. In two reactive bilayer, 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 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 was supported by the National Creative Research Initiative Program supported by KOSEF.

AA8.20

Arrangement of Two Different Types of Nanoparticles from Self-Assemblies of Diblock Copolymer Micelles in the Bimodal Size Distribution for Multifunctional Arrays. Seong Il Yoo[1], Byeong-Hyeok Sohn[2], Sang Hyun Yun[1], Seung Min Jeon[2], Sun Hee Jin[2], Jeong Hwa Choi[2], Wang-Cheol Zin[1] and Jin Chul Jung[1]; [1]Materials Science and Engineering, Pohang University of Science and Technology(POSTECH), Pohang, South Korea; [2]School of Chemistry, NANO Systems Institute, Seoul National University, Seoul, South Korea.

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 onto solid substrates by dip coating or spin coating to form nanostructured 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 the two different sizes. Within the condition that hybridization of large and small micelles was excluded, 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 applicable to various pairs of nanoparticles to generate multifunctional arrays.

AA8.21

Controlling the (In,Ga)As Quantum Dot Patterns by GaAs Substrate Indexes. Shahram Seydmohamadi, Zhiming M. Wang and Gregory J. Salamo; Physics, University of Arkansas, Fayetteville, Arkansas.

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 misorientation miscut towards [011] or [01-1], which are called type-A and type-B respectively. The surfaces under study include singular and vicinal (100), (n11)A and (n11)B - all on one side of stereographic triangle between the (100) and (111) surfaces. While a one-dimensional chain-like ordering of QDs is formed on a singular GaAs (100) and on a slightly misorientated GaAs (100) surface, two-dimensional square-like ordering appears on GaAs (n11)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 miscut toward (111)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 (2x4) reconstruction corrugation. On a high index (711)A surface, the uniformity of the QD chains collapses and the lateral periodicity of the QDs along and perpendicular to the chains changes. We then observe a non-uniform distribution of short QD chains on a (511)A surface, and finally corrugated surfaces on (411)A and (311)A with a random distribution of QDs on the top. The different ordering patterns originate for several physical reasons including the competition between anisotropic surface diffusion, the anisotropic elastic matrix, the affect of the strain field resulting from the buried quantum structures with anisotropic shape, and the formation of QDs on a corrugated (In,Ga)As background for the (311)A and (411)A surfaces. These observations suggest many other possible experiments to explore the control of lateral ordering using self-assembly techniques for novel device application.

AA8.22

Multi-Scale Modeling of Quantum Dot Synthesis in Microemulsion Templates.

Borislava Kostova[1], Georgios N. Karanikolos[1], Yannis G. Kevrekidis[2] and T.J. (Lakis) Mountziaris[1]; [1]Department of Chemical and Biological Engineering, University of Buffalo, Buffalo, New York; [2]Department 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 nanodroplets formed by self-assembly of a ternary 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 dielthylzinc 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 depletion 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 heptane 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 nanodroplet-level models of quantum dot formation are connected to reactor-level operating conditions through the interfacial flux of hydrogen selenide. The results are compared to experimental observations with the purpose of optimizing the quantum dot synthesis process in the experimental system. * G.N. Karanikolos, et al., Langmuir, 20(3), 550-553 (2004).

AA8.23

Vapor-Phase Synthesis of Znse Quantum Dots and Single-Crystalline Nanorods.

Christos Sarigiannidis[1], Taechul Lee[1], Athos Petrou[2] and T.J. (Lakis) Mountziaris[1]; [1]Department of Chemical and Biological Engineering, University of Buffalo, Buffalo, New York; [2]Department of Physics, University at Buffalo, Buffalo, New York.

The vapor-phase synthesis of II-VI nanostructures has several advantages over traditional liquid-phase techniques, including high material purity, elimination of solvents, high throughput, and better compatibility with existing microelectronics industry operations. Synthesis and surface modification of luminescent ZnSe nanocrystals (quantum dots) has been accomplished by reacting vapors 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 vertical opposed-flow configuration. ZnSe nuclei form near the stagnation point by an irreversible reaction between the precursors, and subsequently grow by surface reactions and cluster-cluster coalescence to form nanocrystals that exhibit size-dependent luminescence. To control nanocrystal coagulation and prevent the formation of "hard" polycrystalline aggregates, vapors of 1-pentanethiol were fed into the reactor during synthesis. The thiol molecules did not interfere with nanocrystal formation, but prevented the formation of large coagulated polycrystalline nanoparticles, as demonstrated by HRTEM analysis and by the improved oxidation resistance of the nanocrystals (demonstrated by photoluminescence analysis of stored samples). Detailed process models have been developed and finite element simulations were performed to understand the effects of processing conditions on nanocrystal size and to optimize the experimental process. Vapor-phase synthesis 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-ordered ZnSe nanorod arrays 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.

AA8.24

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 polystyrene-polybutylacrylate nanoparticles, which are monodisperse and have selected sizes from 35-120nm. 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 dictates the self-assembled patterns of the array, which was converted to a polymeric film by thermal curing. The correlation between the tensile strength and the patterns of the arrays will be reported.

AA8.25

Surface Plasmon Absorption and Photoluminescence of Self-Organized Au-Nanopeapodded Silica Nanowires.

Ming-Shien Hu[1], Lu Sheng Hong[1], Ching Hsing Shen[2], Kuei Hsien Chen[2], Bo Wen Ke[3] and Li Chyong Chen[3]; [1]Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan; [2]Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan; [3]Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Recently, the optical properties of noble metal nanoparticle embedded in the dielectric matrices have received growing interest due to the 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 nanoshperes in periodical arrangement along the individual nanowire. The novel Au-peapodded 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 form the composite nanowire using UV-visible absorption measurement and the absorption band was observed to be tailored by the size of Au nanoparticles. Furthermore, the luminescence properties have also been characterized using cathodoluminescence (CL), photoluminescence (PL) and photoluminescence light excitation (PLE) 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.

AA8.26

Multi-Functional Nanolayered Nanoscale Crystals Obtained by Co-Evaporation Followed by MeV Si Ion Bombardment.

Zhigang Xiao, Robert Lee Zimmerman, Iulia Muntele, Bangke Zheng and Daryush Ila; Center for Irradiation of Materials, Alabama A&M University, Normal, Alabama.

Nanoscale multilayer thin films were deposited sequentially by co-deposition of various layered structures such as Au/SiO2/Au/SiO2 as well as BixTe3/Sb2Te3. 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 deposited due to ionization in the track of MeV ion beam can cause localized crystallization. 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. The deposited multilayer 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 3ω 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 NAG8-1933 from NASA. ** Corresponding author: D. ILA; Tel.: 256-372-5866; Fax: 256-372-5868; Email: ila@cim.aamu.edu

AA8.27
Abstract Withdrawn

SESSION AA9: Electronic and Magnetic Behavior
Chair: Younan Xia
Friday Morning, April 1, 2005
Room 2018 (Moscone West)

8:30 AM *AA9.1
FCC Metal Nanocrystals: Shape Control and Assembly. Peidong Yang, Univ. Calif. Berkeley, Berkeley, California.

Recently, the concept of shape control has started to revitalize the centuries-old metal colloidal synthesis. Nanoparticles of various shapes (rods, wires, prisms, cubes), particularly those of silver and platinum, have been prepared using a variety of different methodologies. 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, octahedron, and icosahedron 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.

9:00 AM AA9.2
Ferroelectric/Ferrimagnetic Thin Film Nanostructures of Perovskite-Spinel Phases. Haimei Zheng[1], F. Zavaliche[2,1], Y. Qi[2], L. Mohaddes-Ardabili[2,1], D. G. Schlom[3] and R. Ramesh[1]; [1]Materials/Physics, University of California, Berkeley, California; [2]Materials Science Engineering, University of Maryland, College Park, College Park, Maryland; [3]Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.

Multiferroic materials with simultaneous ferroelectricity and magnetism have recently attracted considerable attention for both fundamental scientific exploration and applications. Multiferroic perovskite-spinel thin film composites, such as BaTiO3-CoFe2O4, BaTiO3-NiFe2O4, BiFeO3-CoFe2O4, BiFeO3-NiFe2O4, etc., were deposited on (001) SrTiO3 substrates using pulsed laser deposition. Films of the different composites have similar nanostructures with CoFe2O4 or NiFe2O4 nanopillar arrays embedded in a BaTiO3 or BiFeO3 matrix, which show three-dimensional heteroepitaxy. All the films have a uniaxial magnetic anisotropy with an easy axis normal to the film plane, which corresponds to the ferrimagnetic nanopillars of spinel phase. We measured the ferroelectric and piezoelectric properties of the films, which correspond to the present of perovskite matrix phase. The system shows a strong coupling of the two order parameters of polarization and magnetization through a stress mediation. This project is founded by an ONR-MURI program at Physics/Materials in UC Berkeley.

9:15 AM AA9.3
Nano-Colonnades: A Novel Technique for Integration of Nanowire Devices. M. Saif Islam[2,1], Duncan R. Stewart[1], Theodore I. Kamins[1], Shashank Sharma[1], Philip J. Kuekes[1] and R. Stanley Williams[1]; [1]Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California; [2]Electrical and Computer Engineering, University of California, Davis, Davis, California.

We demonstrate a novel solution to the problem of interconnecting one-dimensional semiconductor nanowire devices with conventional integrated circuit (IC) elements, employing processes compatible with mass-manufacturing. An 'awning' shaped structure is fabricated using two doped single-crystal layers of Si separated by an insulating oxide layer of precisely known thickness. Using a chemical vapor deposition (CVD) process, arrays of vertically oriented metal catalyzed nanowires, termed "nano-colonnades," are grown from the bottom layer (bottom electrode) and epitaxially connected to the top electrode - resembling the formation of 'stalagmites'. Current-voltage measurements of p-type, boron-doped NWs will be discussed. The technique uses only optical lithography to enable integration of 1D nano-devices with conventional IC's. For the first time, this method helps generate electrically connected nanowires with a very precise length and has potential for applications in the field of optoelectronic nanodevices. In this demonstration, individual electrical access to a large number of nanowires without recourse to nanoprobes or tedious and expensive serial interfacing procedures has been achieved by combining "bottom-up" and "top-down" nanofabrication where self-assembled nanostructures mate to pre-fabricated microstructures.

9:30 AM AA9.4
Electronic Coupling in Self-Assembled Nanocrystal Systems. Yi Cui[1] and Paul Alivisatos[1,2]; [1]Chemistry, UC Berkeley, Berkeley, California; [2]Materials Science Division, Lawrence Berkeley National Lab, Berkeley, California.

Understanding the coupling characteristics of self-assembled nanocrystal systems is important for preparing new types of functional materials. Here we report our recent progress in studying the electronic and photonic coupling in different forms of self-assembled nanocrystal systems. First, semiconductor nanotetrapods are unique self-assembled systems of quantum dots and rods. We demonstrate by single electron transport that either ionic or covalent bonding-type of coupling can exist when the interaction between the quantum dot at the junction and the arm rods is weak or strong, respectively. We also show a new single-electron transistor operation scheme enabled by the unique coupled tetrapod systems: one arm can be used as a sensitive arm-gate to control the electrical transport through the whole system. Second, we developed a facile method for organizing nanocrystals into large-scale device arrays of coupled systems, which incorporate a controlled number of sub 50 nm diameter nanocrystals at lithographically-defined precise locations on a chip and within a circuit.

9:45 AM AA9.5
Designing PbSe Nanowires and Nanorings through Oriented Attachment of Nanoparticles. Dmitri V. Talapin, Chuck T. Black, Cherie R. Kagan and Chris B. Murray; T. J. Watson Research Center, IBM, Yorktown Heights, New York.

High quality PbSe nanowires can be synthesized in a solution through oriented attachment of nanocrystal building blocks. We use high reaction temperatures (190-250C) to allow efficient annealing of crystalline defects and we utilize multicomponent surfactant mixtures to achieve high nanowire uniformity. The synthesis through oriented attachment can produce nanowires with precise control of wire dimensions and morphology. In addition to straight nanowires, zig-zag, helical, branched, tapered nanowires as well as single-crystal nanorings could all be prepared with careful adjustment of the reaction conditions. Depending on the reaction conditions, we observed oriented attachment of {100}, {110} and {111} faces of PbSe rocksalt lattice. To explain the peculiarities of nanowire formation and evolution we propose a model identifying the origin of a dipole moment for PbSe nanocrystals with centrosymmetric rocksalt lattice. Depending on the arrangement of Pb- and Se-terminated {111} facets, the PbSe nanocrystal can lack central symmetry and possess dipole moment along the <100>, <110> or <111> crystallographic directions. The dipolar interactions force PbSe nanocrystals to assemble into chains and fuse into nanowires. Solution-phase synthesis also allows growing coaxial core-shell nanowires. Control of nanowire morphology allows optimization of the material for various applications (e.g., field effect, photovoltaic and thermoelectric devices). Thus, PbSe nanowires can be employed in p-type and n-type FETs and, therefore, can be used in complimentary logic circuits. We propose the novel methods of doping PbSe nanowires both during the synthesis after their integration into devices. The nanowires can be aligned by applying an external electric field, or grown directly on a chip between source and drain electrodes thus facilitating their integration into devices.

10:30 AM *AA9.6
Tunable Plasmonic Nanoparticles and their Array Properties. Naomi Halas, [1]Department of Chemistry, Rice University, Houston, Texas; [2]ECE Department, Rice University, Houston, Texas.

Metallodielectric core-shell nanoparticles (nanoshells) have been shown to possess plasmon resonance frequencies sensitively dependent upon the relative dimensions of their core and shell layers. This plasmon response can be utilized to provide a controlled nanoscale electromagnetic environment for surface enhanced Raman scattering. Nanoshells can also be assembled into large area crystalline arrays. The periodic array geometry induces significant modifications in the plasmonic response relative to nanoshells in dilute films or dense disordered films. Array contributions to the SERS response of adsorbate molecules will be discussed in light of FDTD calculations of the local plasmonic response in the junctions between adjacent nanoparticles in these types of structures.

11:00 AM AA9.7

Magnetic Field-Induced Self-Assembly of Co Nanoparticles.
Guangjun Cheng, Danilo Romero and Angela Hight Walker; Physics, NIST, Gaithersburg, Maryland.

Under the influence of a small magnetic field, Co nanoparticles can assemble into centimeter-long rigorous 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 properties of MFI self-assemblies 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.
Makoto Kuwabara, 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 bariumtitanate 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 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 60 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 pilalrs; this may prove that the barium titanate ceramic pillars fabricated are definitely ferroelectric. In this paper, we describe the possibility of developing ferroelectric photonic 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. Gennady N. Panin[1,2], Tae Won Kang[1], Andrey N. Aleshin[3,4], Andrey N. Baranov[5], Y.-J. Oh[5] and I. A. Khotina[6]; [1]Department of Physics, Quantum-functional Semiconductor Research Center, Dongguk University, Seoul, South Korea; [2]Institute of Microelectronics Technology, Russian Academy of Sciences, Chernogolovka, Moscow distr, Russian Federation; [3]A. F. Ioffe Physical-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russian Federation; [4]Nano System Institute and School of Physics, Seoul National University, Seoul, South Korea; [5]Thin Film Research Center, Korea Institute of Science and Technology, Seoul, South Korea; [6]A. 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 diphenylvinylene), 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.

11:45 AM AA9.10
Self-Assembled Conjugated Polymer Nanowires.
Samson A. Jenekhe, Yan Zhu and Amit Babel; Department of Chemical Engineering, University of Washington, Seattle, Washington.

There is a growing interest in well-defined nanostructured materials such as semiconductor nanowires, polymer nanowires, and carbon nanotubes because of their unique properties resulting from size confinement and restricted dimensionality. In particular, conjugated polymer nanowires have attracted much attention due to their potential applications in nanoelectronics and nanophotonics. In this talk, we will describe the synthesis, self-assembly, nanostructure characterization, photophysical properties, charge transport, and device applications of conjugated polymer nanowires. We have discovered that binary blends of regioregular poly(3-hexylthiophene) and our recently synthesized regioregular poly(4-hexylquinoline) (P4HQ) in dilute solutions self-assemble into crystalline nanowires with a mean diameter of 21 nm and lengths of the order of 1-10 μm. These polymer nanowires were characterized by atomic force microscopy, transmission electron microscopy, and X-ray diffraction. X-ray diffraction studies of the blend nanowires revealed that the two polymers cocrystallize into highly ordered layered structures with an interlayer d-spacing of 16.30-16.40 Å. Ambipolar charge transport was observed in field-effect transistors based on the polymer blend nanowires. A hole mobility of 0.012 cm^2/Vs and an electron mobility of 0.004 cm^2/Vs were observed for the 20 wt% P4HQ blend nanowires. The novel self-assembly approach to polymer nanowires with nanoscale cross-sections and lengths on the order of micrometers from binary blends of conjugated polymers opens up opportunity for exploring new applications of conjugated polymers in nanoscale and molecular electronic devices.