

SYMPOSIUM GG

Mesoscale Architectures from Nano-Units—Assembly, Fabrication, and Properties

November 29 - December 2, 2004

Chairs

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* Invited paper

8:30 AM *GG1.1

Adding a New Dimension in Nanoscale Materials: Metal Nanoparticles with Phase Separated Ligand Shells.

Francesco Stellacci, Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Ligand coated metal nanoparticles are promising nanosize materials for novel electronic and optical devices. Their main strength is in the fact that they combine the advantages of small metals, such as single electron transistor (SET) behavior, together with most of the advantages of the organic ligands that are used to coat them, such as solubility in organic solvents and processability for example via self-assembly methods. Moreover, even complex nanoparticles coated with multiple types of ligands can be synthesized in just one step. Here we present a new family of mixed ligand nanoparticles that shows sub-nanometer patterns (e.g. ridges) on their ligand shell.[1] This unique sub-nano-structuring of their ligand shell provides new properties to the particles. In particular, we focus on silver and gold particles that have ridges composed of hydrophilic valleys and hydrophobic peaks. For the first time we show the ability to control the supramolecular ordering of the ligands on the nanoparticle surfaces. Indeed, by systematically varying the mixture of ligands introduced during nanoparticle synthesis, one can control the resulting surface properties of the nanoparticles. Scanning tunneling microscopy images show ridges 3 Å and 6 Å wide on the ligand shell of nanoparticles. Control of both these parameters is provided by the choice of the ligands and of their molar ratio respectively. We also demonstrate that the nanoparticle ligands interact so as to align the stripes of neighboring nanoparticles over large length scales. The synthetic mechanism that leads to the formation of this supramolecular ordering will be discussed. These particles show unique and unexpected solubility, self-assembly and surface chemistry properties, in particular they show a remarkable resistance to protein nonspecific adsorption. 1 A. Jackson, J. Myerson, and F. Stellacci, *Nature Materials* 2004, 330

9:00 AM GG1.2

Dip-pen Patterning of Peptide Amphiphile Nanofibers. Samuel I. Stupp^{1,2,3} and Hongzhou Jiang¹, ¹Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Chemistry, Northwestern University, Evanston, Illinois; ³Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

Self-assembly of peptide amphiphile (PA) molecules into one-dimensional cylindrical nanostructures has been studied recently in our laboratory. These nanostructures measure a few nanometers in diameter and microns in length, and their peptide segments are presented on the nanofiber surface. Combined with patterning approaches such as dip-pen nanolithography (DPN), evaporation-driven self-assembly of these PA nanofibers offers interesting opportunities to deposit these peptide nanostructures on surfaces. We report here the surface-driven self-assembly of PA molecules using direct patterning techniques to create reproducibly aligned PA nanofibers patterns on silicon substrates. We also show that these nanofibers can retain their alignment when another set of nanofibers of different orientation is created on the first pattern. By tuning patterning conditions, we also also demonstrate the possibility of depositing on surfaces highly aligned close-packed arrays of nanofibers.

9:15 AM GG1.3

Lytropic Liquid Crystal Templating of Mesoporous Hollow Spheres. Paul V. Braun and Alejandro Wolosiuk; Materials Science and Engineering, U. of Illinois at Urbana-Champaign, Urbana, Illinois.

500 nm diameter hollow spheres containing a periodic array of 3 nm pores in a hexagonal lattice in the shell wall were created through liquid crystal templating of the growth of ZnS on colloidal particles, followed by dissolution of the colloidal particle. The colloidal particles were first dispersed into a lyotropic liquid crystal formed from a nonionic surfactant and water that also contained thioacetamide and zinc acetate. Then, ZnS, formed from the reaction of thioacetamide and zinc acetate, heterogeneously deposited in a superlattice structure as defined by the liquid crystal on the surface of the colloidal particles. The mineralized colloidal particles were separated from the liquid crystal, and the colloidal particles were dissolved, resulting in a hollow sphere perforated with a periodic array of nanoholes. Both silica and polystyrene colloidal particles could be used as templates; silica particles are removed with fluoride ions, while polystyrene particles are removed with organic solvents. Initial experiments which demonstrate the sequestering of macromolecules within the

mesoporous hollow spheres while permitting the passage of smaller molecules will be described.

9:30 AM GG1.4

Fabrication of Asymmetrically Coated Colloid Particles by Microcontact Printing Techniques. Olivier J. Cayre, Dpt of chemistry, University of Hull, HULL, United Kingdom.

We developed a novel method for preparation of asymmetrically coated colloid particles by using a microcontact printing technique. Films of water-insoluble ionic surfactants deposited on PDMS stamps were printed onto latex particle monolayers of opposite surface charge in order to produce spherical latex particles of dipolar surface charge distribution. We studied the effects of salt on the aggregation of such dipolar particles in aqueous suspensions. Upon addition of salt, dipolar colloid particles were found to give linear aggregates. We have also extended this microcontact printing technique to the directed assembly of colloidal particles. Microcontact printing of one colloidal monolayer over a latex particle monolayer of opposite charge was used to fabricate particles of complex internal structure. We demonstrated that if the two colloid monolayers consist of particles of comparable sizes, this method allows fabrication of asymmetric particle doublets. When the particle monolayer was stamped with another colloid monolayer of much smaller particle size, complex structures such as half-coated raspberry-like particles were obtained. Possible applications of these asymmetrically coated colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids.

10:00 AM *GG1.5

Directed Assembly of Metal-Organic Nanoarchitectures.

Klaus Kern, ¹Nanoscale Science Department, Max Planck Institute for Solid State Research, Stuttgart, Germany; ²Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The engineering of nanostructures from molecular building blocks provides the unique advantage that organization and functionality can be manipulated by chemical design. With the thoughtful choice of the individual molecular constituents highly organised supramolecular architectures can be realized providing tailor-made properties. In addition, molecular nanostructures offer a natural interface to the biological world and can be employed to explore the coupling of inorganic structures to living organisms or cells and to implement biological principles in devices and sensors. In this talk I demonstrate the use of specific metal ligand interactions for the construction of hybrid nanoarchitectures. The first example addresses the use of large biomolecules like the tobacco mosaic virus (TMV) for nanotemplating. The well-defined chemical groups at specific locations of the coat proteins of the virus can act as ligands for metal ions. We use this chemical functionality for the selective growth of metal nanowires and/or coatings from metal ion solutions. The second example discusses the construction of complex metal-organic nanoarchitectures at surfaces using concepts from coordination chemistry. Well-ordered supramolecular structures and coordination networks with specific topologies and high structural stability are fabricated by self-assembly of polyfunctional organic molecules and Fe atoms at single crystal surfaces.

10:30 AM GG1.6

Uniform mesoporous silica films with arrays of oriented cylindrical pores. Sivakumar Nagarajan¹, Mingqi Li³, Rajaram A. Pai², Craig Weinman³, Christopher K. Ober³, Thomas P. Russell¹ and James J. Watkins²; ¹Polymer Science and Engineering, University of Massachusetts, Amherst, Amherst, Massachusetts; ²Chemical engineering, University of Massachusetts, Amherst, Amherst, Massachusetts; ³Material science and engineering, Cornell University, Ithaca, New York.

Ordered mesoporous metal oxide films are of enormous interest for applications in catalysis, separations, photonics, electronics, sensing and detection devices. One unresolved challenge has been the fabrication of robust films with cylindrical pores aligned perpendicular to the plane of the substrate. Such an arrangement renders the pore structure accessible for the intended application. We have developed a novel approach to mesoporous films in which metal oxide precursors are rapidly diffused through and selectively condensed within one domain of a preorganized block copolymer film that is dilated with supercritical carbon dioxide. Using this two-step process, the structural details of the block copolymer template are transferred to the metal oxide network with high fidelity. Thus structures imparted wholly in the block copolymer during template formation carry over into the mesoporous silicate enabling prescriptive control of film structure by template manipulations. Recently, the rapid preparation of micro phase-separated block copolymer films with cylindrical domains oriented normal to the substrate surface using controlled solvent evaporation has been described. Here, we report the replication of these oriented templates to yield uniform

silica films with an array of oriented and accessible cylindrical pores. The process is rapid, efficient and easily extendable to other metal oxides. 1. Pai et al., Science 2004, 303, 507.

10:45 AM **GG1.7**

Patterning Complex Multi Component Structures with Ferroelectric Nanolithography. Dawn Bonnell, Xiaojun Lei and Dongbo Li; Materials Science, University of Pennsylvania, Philadelphia, Pennsylvania.

Complex structures are fabricated by independently locating multiple nanostructures in pre determined positions, overcoming one of the limitations of self assembly in a process that operates on multiple types of compounds simultaneously. Atomic polarization in ferroelectric perovskites is manipulated to control surface electronic structure and local chemical reactivity. Paradigms for ferroelectric domain patterning using scanning probe microscopy, electron beams lithography and microcontact stamping are presented. Photo reaction of inert and reactive metal nanoparticles, complexing with functionalized porphyrins and peptides, and semiconductor nanoparticles allows assembly into configurations that yield nanodevices, such as optoelectronic switches and modulators. Sequential and simultaneous patterning of multiple compounds will be demonstrated.

11:00 AM **GG1.8**

Directed Crystallization of Functionalized Molecules on Nanopatterned Self-Assembled Monolayers. Ashok Kakkar, Florence Quist and Adam Dickie; Chemistry, McGill University, Montreal, Quebec, Canada.

Surface chemistry offers a unique opportunity to assemble desired molecules into organized and controlled architectures that can initiate crystallization by molecular recognition. Such a methodology offers tremendous potential in addressing key issues related to controlled polymorphism in pharmaceutical solids and construction of smart materials. We have recently developed a serial templating methodology to construct patterned nanoassemblies on semiconductor substrates. These self-assembled thin films can direct nucleation and crystal growth of functionalized molecules using a combination of molecular recognition and supramolecular interactions. The resulting solid state morphologies can be easily tailored by subtle variations in self-assembling patterning components. A detailed examination of combining bottom-up chemisorption process with supramolecular association in controlling polymorphism in solids will be presented.

11:15 AM **GG1.9**

Solution Stamping Nano-Lithography for Patterned Deposition of Inorganic Films. Nolanne A. Chang, Julia W.P. Hsu, Jacob J. Richardson and Paul G. Clem; Sandia National Laboratories, Albuquerque, New Mexico.

In solution stamping nano-lithography (SSNL), an elastomeric stamp containing relief patterns is first "inked" with a sol gel precursor solution of inorganic (functional oxide or ceramic) materials, and then placed on a surface to transfer this "ink" from the stamp to the substrate. Due to the flexible mechanical properties of the elastomeric material, the stamp forms a conformal contact with the surface. Ink transfer only occurs at locations where the stamp contacts the surface because of the stamp morphology. Hence, the resulting patterns on the substrate mirror the stamp relief structures. The stamped precursor patterns are then processed following standard procedures to convert them to the final composition of the inorganic materials. If a lattice-matched substrate is used, the patterned thin films may be epitaxially registered to the substrate. Epitaxial deposition of 100nm thick superconducting YBCO films has been demonstrated with this method to date. Research in pushing lateral resolution downward toward 200nm will be reported. In addition, initial work toward junction fabrication and top-down patterned self-assembly of nanoparticles will be discussed. 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 ***GG1.10**

Fabrication of 3D Nanoarchitectures by Way of Nanocopying of Natural Substances: Copying of DNA Strand and Artificial Fossils. Toyoki Kunitake^{1,2}, Shigenori Fujikawa¹, Rie Takaki¹ and Jianguo Huang¹; ¹Frontier Research System, RIKEN, Wako, Saitama, Japan; ²The University of Kitakyushu, Kitakyushu, Fukuoka, Japan.

We define nanocopying as "copying of nanometer-size objects such as molecules, supermolecules, nano-particles and surface morphologies with nanometer precision" (1). There are two types of copies - positive copy and negative copy. Positive copy with the nanometer precision should be achieved by covering of a given template with ultrathin (nanometer-thick) layers and subsequent template removal. In

contrast, negative copy is formed as a result of stamping and void filling (molding). It is also obtained by embedding/removal of molecular templates in copying matrices. Formation of inverse opal is a typical case of negative copy. In order to achieve nanometer precision, the matrix material has to be uniform, shape-adaptable at the nanometer precision, and self-supporting. The former property is essential for recreating morphological characteristics of templates, and the latter is required for maintaining 3D structural mimics of the copied object. Infinite amorphous solids such as organic polymers, inorganic glasses and metals may be candidate materials for this purpose. Certain metals may produce ultrathin layers with complex morphological characteristics of templates. However, metal nanosheets and polymer nano-layers are probably not robust enough for sustaining 3D structures of nano-sized copies. The surface sol-gel process can satisfy the above requirements of the copying material. We applied this method to natural substances. Cellulose fibers possess surface hydroxyl groups, and filter paper provides a suitable vehicle for the process. Upon removal of the template paper, the overall shape of the original filter paper was retained except for a little shrinkage in size, and the original morphology of the intertwined fibers was faithfully replicated by titania nanotubes(2). As another example, we conducted nanocopying of DNA strands (3). Lambda DNA molecules were spread on a solid substrate, and subjected to the surface sol-gel process with titanium butoxide. The occluded DNA chains cannot be decomposed by DNase and can be removed by oxygen plasma. The resulting nanotubes were clearly observed by TEM. (1) S. Fujikawa, T. Kunitake, Analytical Chimica Acta, 504(2004), pp.1-6 (2) J. Huang, T. Kunitake, J. Am. Chem. Soc., 125(2003), pp. 11834-11835 (3) R. Takaki, S. Fujikawa, T. Kunitake, in preparation

SESSION GG2: Nanotemplating for Meso-scale Assembly II

Chairs: Paul Braun and Mauricio Terrones
Monday Afternoon, November 29, 2004
Room 311 (Hynes)

1:30 PM ***GG2.1**

Controlling Emergent Nanoscale Structure in Materials

Synthesis. Yiyang Wu¹, Guosheng Cheng¹, Kirill Katsov², Scott W. Sides³, Jianfang Wang¹, Jing Tang², Glenn H. Fredrickson^{2,3}, Martin Moskovits¹ and Galen D. Stucky^{1,2}; ¹Dept of Chemistry & Biochemistry, UCSB, Santa Barbara, California; ²Materials Dept, UCSB, Santa Barbara, California; ³Dept of Chemical Engineering, UCSB, Santa Barbara, California.

A fundamental pursuit in materials science is control of molecular assembly by changing the synthesis environment without modification of the precursor chemistry or other reaction conditions. In a physically confined environment, interfacial interactions, symmetry breaking, structural frustration, and confinement-induced entropy loss play dominant roles in determining molecular organization. This talk will illustrate the concept of emergent structures with results on confining the assembly of silica-surfactant composite mesostructures inside cylindrical alumina nanochannels. Varying the diameter of the nanochannels spontaneously produces a variety of architectures, including unprecedented chiral silica mesostructures with single-helix and double-helix geometries. Upon tightening the confinement, a transition occurs in the mesopore morphology from a cylindrical to a spherical cage-like geometry. Additional nanoscale sculptured configurations are accessible by modifying the confinement constraint. The mesostructures produced by confined synthesis can be used for the creation of functionalized high pore density membranes and as templates for fabricating highly ordered mesostructured nanowires and nanowire periodic arrays with metallic or semiconducting functionality.

2:00 PM **GG2.2**

Mesostructure Control of 1D Mesoporous Silica within Anodized Alumina Membrane.

Rong Kou¹, Donghai Wang¹, Zhenzhong Yang² and Yunfeng Lu¹; ¹Chemical and Biomolecular Engineering, Tulane university, New Orleans, Louisiana; ²State Key Laboratory of Polymer Physics and Chemistry Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Science, Beijing, China.

Cooperative self-assembly of silicate and surfactant can generate liquid crystal structured mesophases (e.g., hexagonal, lamellar or cubic structure), thus forming highly ordered mesoporous silica after removal of surfactants. Due to the unique mesoscale structures, various morphologies, and controllable surface properties, mesostructured silica or composite materials have been applied in many fields such as catalysis, separation, sensor, optical materials, templates synthesis, etc. It is increasingly important to control mesoporous materials in a small feature such as micro/nano scale size for its potential device applications. In this work, we have

investigated the self-assembly behavior of silicate/surfactant confined within hydrophilic anodized alumina membrane and obtained 1D mesoporous silica with a variety of mesostructures distinct from both bulk and previously reported 1D mesoporous materials. With increasing surfactant concentration in the precursor solution, mesostructures of 1D mesoporous silica were changed from disorder, cubic, spiral hexagonal to circular lamellar structure. As the size of mesophase is down to nanoscale, interfacial property also plays prominent roles on the self-assembly behavior of silicate/surfactant. Liquid-solid interface at the pore surface serves as a nucleating surface for inward growth of silicate/surfactant mesophase radially till the pores are completely filled. The circular curvature of nucleating surface result in circular growth of hexagonal or lamellar liquid crystalline mesophase, and therein forming the corresponding spiral hexagonal and co-central lamellar structured 1D mesoporous silica. With incorporation of shearing field in growth of mesophase within alumina pore channels, straight hexagonal mesoporous structure perpendicular to the membrane plane were achieved. This research will bring the insight into nanoscale confinement effect on cooperative inorganic-organic self assembly behavior. We expect that this new unique structured mesoporous silica arrays will be applicable to templated synthesis, separation and other applications.

SESSION GG3/C2: Joint Session: Emerging Paradigms
in Nanopatterning and Mesoassembly
Chairs: Paul Braun, Eric Lin and G. Ramanath
Monday Afternoon, November 29, 2004
Room 311 (Hynes)

2:30 PM *GG3.1/C2.1

Mesoscale Architectures from Nanounits: Assembly, Fabrication. A. Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

This talk will focus on the use of creation of new shapes and topologies of nanocrystals. Nanocrystals can act as a fundamental unit for chemical transformation. For example, through studies of interdiffusion between two components in a particle, we have learned how to make hollow inorganic nanocrystals. A second example concerns controlled branching, which enables us to create new types of heterostructures. Finally, very recent work in which we employ cation exchange to alter the chemical composition of nanocrystals will be described.

3:00 PM *GG3.2/C2.2

The Future of The Semiconductor Industry: Top Down or Bottom Up? Ralph R. Dammel, AZ Electronic Materials, Clariant Corporation, Somerville, New Jersey.

The rapid rise of the semiconductor industry is without doubt one of the main success stories of modern industrial development. At the heart of the industry's success is its ability to keep shrinking device sizes exponentially over time according to Moore's Law, resulting in ever decreasing cost per function. As of today, the industry's Roadmap looks out 14 years, until 2018, without forecasting a slowdown of Moore's Law. From the technical side, we have a pretty good understanding what needs to be done to pattern the 45 nm features the Roadmap requires at the end of this decade, but there are still fundamental questions to be resolved for the years further out. In particular, some question whether the patterning capability of the chemical amplification mechanism (which underlies the dominant class of photoresists today) can be extended beyond 50 nm. Even if the technical hurdles are overcome, the investment cost of photolithography and manufacturing future chip generations in general may become so high that the market will be unable to bear it. Such an economic end to Moore's Law could occur even if it is technically feasible to make smaller devices and although the cost per function would continue to decrease. Following an outline of present-day photolithographic technology, this paper will explore a way out of the coming crisis that may lie in the use of some form of nanoimprint technology, which presently still is in an early stage but has the potential to be substantially cheaper than conventional photolithography.

3:30 PM *GG3.3/C2.3

Unconventional Nanofabrication and Meso-Scale Self-Assembly. George M. Whitesides, Logan McCarty, Qiaobing Xu, Byron Gates, Brian Mayers, Lara Estroff and Vijay Krishnamurthy; Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Chemistry, with stimulus from biology, is beginning to develop a range of new concepts for the fabrication of mesoscale systems by templated self-assembly from nanoscale components: these include a range of types of self-assembly, printing, molding, microfluidic

patterning, electrochemistry, sectioning, and related techniques designed to make it possible to design complicated structures having electrical, optical, biological or magnetic functionality and to assemble and replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application.

4:00 PM *GG3.4/C2.4

Massively Parallel Dip Pen Nanolithography. Chad A. Mirkin, Chemistry, Northwestern University, Evanston, Illinois.

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic nanoelectronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:30 PM *GG3.5/C2.5

Nanoimprint Lithography (NIL), Laser-Assisted Direct Imprint (LADI) And Lithographically-Induced Self-Assembly (LISA). Stephen Y. Chou, Department of Electrical Engineering, NanoStructure Laboratory, Princeton University, Princeton, New Jersey.

The talk will present several innovative nanopatterning methods and their advancements developed at NanoStructure Lab at Princeton. The first is nanoimprint lithography (NIL), which patterns a resist by physical deformation using a mold. We will present our demonstration of sub-12 nm pitch, sub-5nm feature size, sub-20 nm alignment (one sigma), and large-area uniformity in NIL, as well as various NIL tools. The second is laser-assisted direct imprint (LADI), which directly patterns nanostructures on hard material surface, chemical-free and without etching. LADI uses an excimer laser, shining through a transparent mold, to melt a thin surface layer of a hard material, and then presses a mold into the molten material. We will show our achievements of sub-10 nm features imprinted in Si, LADI in SiC and metals (Au and Cu), and new applications of LADI in wafer planarizations. Finally, we will present lithographically-induced self-assembly (LISA), where self-assemblies of nanostructures are guided by much large patterns and can achieve single domain over a large area. Furthermore, we used LISA to achieve self-alignments and self-assembly (SALSA) between the connections and electronic devices to create random access-electronic devices array. The work was supported in part by DARPA and ONR. The author acknowledges the contributions of other members of NanoStructure Lab at Princeton to the presentation materials.

SESSION GG4: Bioinspired Synthesis, Templating and Assembly
Chair: Paul Braun
Tuesday Morning, November 30, 2004
Room 311 (Hynes)

8:30 AM *GG4.1

New methods for the synthesis of nanomaterials. Murali Sastry, Materials Chemistry Division, National Chemical Laboratory, Pune, India.

Wet-chemical methods for the synthesis of nanomaterials are extremely popular for a variety of reasons. Nanoparticles over a range of chemical compositions, sizes and shapes can be routinely synthesized in both aqueous and non-polar organic solutions with a variety of surface modifiers that include standard surfactants and biomacromolecules. However, many processes for nanoparticle synthesis often involve the use of toxic chemicals, which are increasingly becoming taboo. Realizing that some of the most exquisite inorganic nanostructures are synthesized by biological systems such as diatoms and bacteria, nanoscience researchers are turning towards biology for inspiration. In the first part of the talk, I will cover the work carried out in my laboratory on the use of fungi, actinomycetes and extracts from various plant parts in the synthesis of nanoparticles of different compositions. We have been successful in synthesizing nanoscale metals, sulphides and oxides by appropriate choice of microorganisms and examples will be given to illustrate this new approach [1]. While achieving tolerable nanoparticle monodispersity continues to be an important issue with biological nanoparticle synthesis methods, shape modulation may be one aspect

where select biological methods appear to be superior to chemical synthesis methods. Bubbles have fascinated man for a very long time. In the second part of my talk, I will show that liquid foams (a dense assembly of bubbles) may be used for the synthesis of nanoparticles over a range of chemical compositions. This is accomplished by ion entrapment in the foam followed by chemical reaction resulting in the formation of nanoparticles in the foam [2]. Liquid foams possess a very complex structure and present nanoscale reactors of variable geometry that may be used creatively in the synthesis of nanoparticles of different shapes. An important advantage of the foam-based method is the in-built scale-up facility that could be of value for commercial scale production of nanomaterials. [1] M. Sastry, A. Ahmad, M.I. Khan, R. Kumar, 'Microbial Nanoparticle Production' in Nanobiotechnology : Concepts, Applications and Perspectives (ed. C.M. Niemeyer and C.A. Mirkin), Ch.9, p.126 (Wiley-VCH, Weinheim, 2004). [2] S. Mandal, S.K. Arumugham, S.D. Adyanthaya, R. Pasricha, M. Sastry, J.Mater.Chem. 2004, 14, 43.

9:00 AM *GG4.2

Genetic Approaches to Material Assembly. Stanley Brown, Dept. of Mol. Cell Biology, University of Copenhagen, Copenhagen, Denmark.

Proteins play amazingly diverse structural and catalytic roles in biological systems. We wish to explore the mechanisms by which proteins can perform similar functions in the formation and assembly of inorganic materials. We have instituted an approach based on cell-surface display to investigate these mechanisms. In a strategy similar to phage display, we express random polypeptides on the surface of the bacterium *Escherichia coli*. A feature of these strategies is the ability to recover individuals displaying rare properties from initial populations comprising millions or billions of different members. The recovery of rare individuals results from the observation that a polypeptide adhering to the selected surface allows adhesion of the bacterium expressing the gene for that polypeptide to the selected surface. Our population was designed to simplify genetic analyses of the recovered polypeptides. We find the interactions of proteins with inorganic materials show many similarities with interactions typical of proteins and other biomolecules. First, we have found polypeptides that distinguish surfaces of identical atomic composition but different spatial orientation. Second, the polypeptides we have found that modulate gold crystal formation and dissolution utilize common enzymatic mechanisms. We imagine the diverse adhesive, structural, reactive and catalytic traits of proteins can provide new solutions to nonbiological problems.

9:30 AM GG4.3

Towards the Formation of Ordered Quantum Dot Arrays: Interactions with Amino Acids, Polypeptides and Proteins. Marcus Jones, Shi-You Ding, Yong-Hyun Kim, Shengbai Zhang, Arthur J. Nozik, Michael E. Himmel and Garry Rumbles; National Renewable Energy Laboratory, Golden, Colorado.

We have developed bio-inspired strategies for controlling the assembly of one and two-dimensional quantum dot (QD) arrays, either on substrates or as free entities in solution. Regular structures, with inter-QD distances small enough to facilitate energy transfer, have been created by exploiting the natural substrate-binding and self-assembling properties displayed by certain proteins. A detailed understanding of the interaction of amino acids with the surface of QDs was essential for this work. Studies have shown that natural and modified amino acids can bind to the surface of (CdSe)ZnS (core)shell QDs. Amino acids not only confer water solubility to QDs, but studies of these interactions also offer insights into the most suitable linkers for binding proteins and polypeptides to the QD ZnS surface. We have specifically investigated the three most nucleophilic amino acids: cysteine, lysine, and histidine; containing thiol, primary amine, and imidazole groups, respectively. Using steady-state and time-resolved photoluminescence (PL) spectroscopy, we have studied the efficiency with which these species bind to the QD surface, the stability of the water-soluble product, and the ability of the group to passivate QD surface states. Both lysine and histidine were found to produce aqueous colloidal QD solutions with PL quantum efficiencies comparable to the standard tri-octyl phosphine oxide (TOPO)-capped species. Calculations show that these amino acids have the strongest surface binding energy (in the absence of solvent) of all the amino acids tested. Whereas stable histidine conjugates form readily in neutral pH conditions, strongly basic conditions are required for the preparation of lysine conjugates, which precludes the use of lysine to link QDs to proteins that denature under such conditions. Cysteine was also able to bind to QDs and produce metastable solutions at near-neutral pH levels; however, thiol oxidation occurred quickly to form cystine. Cystine, a disulfide-containing compound, is a poor ligand and caused QD precipitation. Oxidation was successfully inhibited with dithiothreitol or by using non-natural cysteine derivatives. The ability of these amino acids to act as suitable capping groups has enabled us to direct the interaction of QDs with proteins

in a number of novel ways. The amino acid ligand can be biotinylated and incubated with avidin-containing proteins to form an irreversibly bound, QD-protein bioconjugate. Alternatively, genetic modification of the N- and C-termini of self-assembling proteins with suitably nucleophilic peptide chains can facilitate a more selective binding of proteins directly to the QD surface. We present PL data and striking microscopy images that show these approaches afford excellent control over the construction of QD arrays or chains.

9:45 AM GG4.4

Scanning Probe Microscope Investigations of the Self-assembly of Genetically Engineered Polypeptides for Molecular Interconnect Applications. Narendra Rana¹, Christopher Kossow¹, Autumn Carlsen¹, Natashiya Topilina², Vladimir Ermolenkov², Seiichiro Higashiya², Igor Lednev², John Welch², Eric T. Eisenbraun¹, Robert E. Geer¹ and Alain E. Kaloyeros¹; ¹College of Nanoscale Science and Engineering, University at Albany - SUNY, Albany, New York; ²Department of Chemistry, University at Albany - SUNY, Albany, New York.

As integrated circuit (IC) features continue to decrease in size and pitch the performance of conventional materials for on-chip interconnects may be severely limited by fundamental physical processes. An example includes increased resistivity of metal lines due to surface scattering at feature dimensions below the electron mean free path (~40 nm for Cu). Future nanoscale interconnect candidates may need to exploit novel conduction mechanisms such as ballistic electron transport requiring a high degree of intra-molecular order. This highlights the need for such nanoscale interconnects to exploit the phenomenon of self-assembly. Self-assembly of interconnect materials may also aid in avoiding the dimensional variability inherent in top-down processing. Pursuant to these requirements carbon nanotubes and bio-inspired materials are being studied extensively for such device and interconnect applications. Along this line we have investigated genetically engineered polypeptide molecules that exhibit beta-sheet protein folding as a platform from which to synthesize self-assembling conducting networks. These molecules have additional advantages such as monodispersity and synthetic controllability. The polypeptide under investigation consists of an alanine and glycine {-(ala-gly)₃-} backbone. Successive beta-turn groups consist of tyrosine, glutamic acid, histidine, and lysine groups yielding salt-bridged beta-turns on one side of the sheet opposite phenyl-containing turns. Scanning probe microscopy (SPM) of these polypeptide molecules on different substrates such as nickel and highly ordered pyrolytic graphite (HOPG) has revealed the formation of secondary intra-molecular assembly into a novel fibril structure. Synthetic scaling of the 'length' of the polypeptide molecule leads to a corresponding scaling of the observed fibril width. Comparison with beta-sheet dimensions from molecular modeling permits an unambiguous determination of the beta-sheet orientation within the fibril. Coupled with resonance Raman spectroscopy analysis of the polypeptide material in solution we conclude that the fibril represents an end-to-end planar stacking of the polypeptide beta sheets. The effects of different parameters affecting the self-assembly such as pH, concentration and temperature have been studied which lays the foundation for further progress in understanding the nature of folding in these materials and the feasibility for their modification for electrical conduction.

10:15 AM *GG4.5

Hierarchical Self-Assembly Through Electrostatic Interactions. Gerard Wong,¹Materials Science & Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois; ²Physics, University of Illinois at Urbana Champaign, Urbana, Illinois.

Charged biological macroions of varying complexity (such as membranes, polyelectrolytes, and globular proteins) can be collectively organized through the interplay of electrostatics and entropy. These interactions are quite general, since all nucleic acids, all cell membranes, as well as most proteins and sugars are charged. The macroions which self-assemble are frequently oppositely-charged, but in contrast to intuition, they can be like-charged as well. We will focus the discussion specifically on our recent work on interactions between charged biopolymers and charged membranes. Early examples include complexes of anionic DNA and cationic lipids for non-viral gene therapy. We have examined the general assembly of such complexes by investigating other forms of anionic biopolymer-cationic membrane assembly comprised of biopolymers of different charge, flexibility, and radii. Liquid crystalline complexes can also be formed from like-charged biopolymers and membranes, using interactions mediated through small molecule cations. Finally, we show that molecular details of DNA can be imprinted onto CdS nanorods using biopolymer-membrane complexes.

10:45 AM *GG4.6

Biomolecular Nanolithography: Scaffold Approaches to Organized Nanoparticle Structures. James E. Hutchison, Gerd H.

The ability to pattern nanometer-scale structures through convenient, highly-parallel processes is an important challenge in nanoscience. For electronic and optical applications of nanostructures in nanoelectronics, nanophotonics, and spintronics, the ability to precisely control the feature sizes and the spacing between the individual features at the nanometer- or Angstrom-level is necessary in order to manipulate the electronic and optical interactions (e.g. tunneling barriers, capacitive coupling, wave function overlap, energy transfer) between neighboring structures and thus tune device function and properties. In addition, the integration of these patterns into hierarchical structures that provide useful interfaces to the macroscopic world is important. Our approach to addressing these challenges is based upon functional group-directed assembly of well-defined nanoparticle building blocks. Using this approach we are pursuing 1-, 2- and 3- dimensional structures derived from gold nanoparticles. In this presentation, we will focus primarily on our efforts to organize ligand-stabilized gold nanoparticles onto DNA templates to form extended 1- and 2-dimensional assemblies. One of the key features of scaffolding approaches that rely on DNA templates is the precision with which the 2- and 3-D structures can be controlled. In addition to particle size and interparticle spacing, the pattern and size of the assembly can also be controlled. The spacing between neighboring nanoparticles can be tuned at the molecular level by utilizing nanoparticles possessing ligand shells of varying thickness to achieve Angstrom-level resolution at spacings of 1.5, 2.1, and 2.8 nm. The length of the resulting monodisperse nanoparticle polymers can be controlled precisely through choice of the DNA template (e.g. using monodisperse DNA samples comprised of 250 base pairs (85 nm) and 500 base pairs). The subsequent assembly of these chains into extended, two-dimensional superlattices on surfaces provides a striking demonstration of how the monodisperse nature of these nanoparticle chains influences the properties of the material. The use of specifically-defined DNA templates to interface the nanoparticle assemblies for electrical characterization will also be discussed.

11:15 AM **GG4.7**

Assembly of Virus on Nanometric Chemical Patterns.

Chin Li Cheung¹, Raymond Friddle¹, Melinda Tonks¹, Alexandr Noy¹, Julio Camarero¹, Jim J. De Yoreo¹, Anju Chatterji², Tianwei Lin² and John E. Johnson²; ¹BioSecurity and NanoSciences Laboratory, Lawrence Livermore National Laboratory, Livermore, California; ²Molecular Biology, The Scripps Research Institute, La Jolla, California.

One of the challenges associated with assembly of nanoscale elements into mesoscale structures is to develop a fundamental understanding of the physical principles underlying assembly, particularly in solvent-based systems where covalent and/or ionic bonding are of little significance and hydrophobic forces are more important. Because viruses can be genetically manipulated to select for specific materials, recently much attention has been given to their use as vehicles for assembling metal, metal oxide, and semi-conductor nanoparticles. What has gone essentially unrealized is that virus particles also present atomically precise tools to study the physics of assembly in symmetrical nanoscale systems. Properties of icosahedral viruses in particular, such as their symmetrical geometry and the surface charge distribution, allow their use in building complex hierarchical structures at the mesoscale. Here we present a study of the virus-assembling process with genetically engineered Cowpea Mosaic virus (CPMV) on nanometric patterns of chemical linkers made by nanolithography. The surfaces of these viral particles are functionalized with either cysteine residues or histine-tags (His-tag), which allow the attachment of the virus to the chemical patterns either through covalent linkage on patterns with maleimides groups or metal coordination complex linkage on patterns with nickel-chelating nitrilotriacetic acid (Ni-NTA) groups correspondingly. In the latter case, to explore the effect of virus' mobility on assembly, we modulated the virus-surface binding strength by additions of competing metal coordinating ligands such as imidazoles. To investigate the role of virus flux and inter-viral interactions, we varied the virus concentration and the solvent composition through addition of polyethylene glycol. The effect of linear chemical patterns of different lengths on the resulting assembled structures was also examined. Force microscopy was used to investigate the degree of ordering, packing geometry, assembly kinetics, and inter-viral potential. The results show clear dependencies on the various parameters and will be presented within the framework of assembly principles borrowed from small molecule systems. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

noindent 11:30 AM **GG4.8**

Directed Assembly of Nanomaterials Based on Analyte-Specific DNazymes. Yi Lu and Juewen Liu; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

A grand challenge in nanoscale science and engineering is how to transform self-assembly of simple structures into directed assembly of highly defined complex mesostructures. Introducing biomolecules into nanostructures provide an opportunity to meet such a challenge, as the biomolecules can be programmed to turn on and off the assembly with high spatial and time resolution and under constant temperature and pressure. DNazymes, or catalytic DNA molecules, are ideal choices for directed assembly of nanomaterials, as they are consist of DNA that can be programmable genetically and possess enzymatic functions that are specific to the present of an analyte. Since its discovery in 1994, a number of DNazymes that are specific for a wide range of analytes have been obtained through combinatorial selection techniques such as in vitro selection and evolution. We have demonstrated the use of DNazymes for directed assembly of gold nanoparticles in which the assembly state is highly dependent on the presence of specific analytes such as Pb²⁺ or adenosine. The nanomaterials assembly states can be turned on or off. And the degree of assembly can also be controlled by careful use of DNazymes with different sequences and activities. In addition to advancing directed assembly of nanomaterials, the resulting system has been used as highly sensitive and selective colorimetric biosensors for metal ions and organic molecules. The methodology is generally applicable to almost any chosen analytes and thus significantly expands its impact in both nanotechnology and other fields and technologies.

11:45 AM **GG4.9**

Self-assembly between DNA and anionic membranes.

Hongjun Liang¹, Thomas Angelini² and Gerard C.L. Wong^{1,2}; ¹Dept. of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We investigate the structure and interactions between anionic polyelectrolytes and anionic membranes, using self-assembled complexes between DNA and anionic membranes. Like-charged DNA and anionic membrane generally repel each other, but in the presence of divalent ions, they can self assemble into complexes with a rich polymorphism of phases. The structure of the complex is determined by the charge density of the membrane as well as the global counterion concentration. For example, the system can adopt lamellar or inverted hexagonal phases comprised of DNA and membrane, depending on the number of condensed ions. Preliminary results on the phase diagram of this system and its potential applications will be discussed.

SESSION GG5: Nanowire and Nanotube Assembly

Chairs: Xavier Blase and Mauricio Terrones

Tuesday Afternoon, November 30, 2004

Room 311 (Hynes)

1:30 PM ***GG5.1**

Fabrication of Complex Carbon Nanotube Architectures.

Pulickel M. Ajayan, Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

The talk will focus on the recent developments in our laboratory on the fabrication of carbon nanotube based architectures tailored for various applications. Various organized architectures can be fabricated using relatively simple processes and some of these structures can be used for novel applications such as sensors, adhesive coatings, filters and polymer based thin film composites. Complex 2-D and 3-D structures can be controllably built from nanotube units. Our efforts on the strategies of growth and manipulation of nanotube-based structures will be discussed.

2:00 PM **GG5.2**

Monolayers of multiwall carbon nanotubes.

Vladimir A. Samuilov¹, Jean Galibert², E. Couteau³, M. Seo³, L. Forro³, J. Sokolov¹ and M. Rafailovich³; ¹Materials Science, SUNYSB, Stony Brook, New York; ²Laboratoire National des Champs Magnetiques Pulses, Toulouse, France; ³Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Monolayers (dense arrays) of functionalized multiwall carbon nanotubes (MWCNT) were assembled using the Langmuir-Blodgett (LB) technique in contrast to the standard morphologies of the samples of arrays of nanotubes involving definitions of bundles (ropes), mats, networks, etc., based on hardly controlled deposition from organic solvent dispersions of pristine nanotubes. The method we propose offers a radical departure from the existing methodology due to the possibility to cover large surfaces with dense thin films of

carbon nanotubes. To our knowledge, up to now, there is no experimental data on electrical and magneto-transport properties characterization of dense monolayers manufactured using LB assembling of functionalized nanotubes. The obtained layers (dense arrays) of MWCNTs could be used for new applications in chemical and biosensors, controlled by the electrical transport. The nanotubes samples on the electrodes with finger-shape geometry have shown low resistance (<1kOhm at room temperature) and a weak power law dependence of the resistance on temperature in the range $T=4.2-300$ K. The temperature dependences of the resistance represents a power-law in the temperature range lower than 100K with the exponent (-0.22). While the power law can fit the temperature dependence of the resistance in MWCNT, it is suggested the formation of a Luttinger liquid. A negative magnetoresistance, as a characteristic of the weak localization state was observed. In addition to the high magnetic field negative magnetoresistance we observed a positive magnetoresistance at low fields as a signature of weak antilocalization.

2:15 PM GG5.3

Atomic Step-Templated Formation of Single-Wall Carbon Nanotube Patterns. Ariel Ismach¹, Lior Segev¹, Ellen Wachtel² and Ernesto Joselevich¹; ¹Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; ²Chemical Research Infrastructure, Weizmann Institute of Science, Rehovot, Israel.

Following recent advances in the control of nanowire electronic properties, non-lithographic organization of nanowire arrays on surfaces remains a critical prerequisite for the large-scale fabrication of nanoscale circuitry. Current strategies include the application of physical means, such as electric fields, gas and liquid flows, and superlattices, as well as chemical means, including self-assembly and biotemplated assembly. Step decoration is another attractive chemical approach that exploits the selective deposition of atoms, ions or molecules at the oriented, periodic steps present on high-index crystalline surfaces. The general scheme, however, where nanowire growth propagates transversally from the steps, is not compatible with nanowire materials that form by axial growth mechanisms, such as carbon nanotubes. Here we demonstrate and characterize the longitudinally propagating decoration of atomic steps by a nanowire material. Single-wall carbon nanotubes, catalytically produced on miscut C-plane sapphire wafers, grow along the 2 Å-high atomic steps of the vicinal α -Al₂O₃ (0001) surfaces, yielding highly aligned, dense arrays of discrete, nanometer-wide, conducting or semiconducting wires on a dielectric material. The nanotubes reproduce the atomic features of the surface, including steps, facets and kinks. The direction, spacing and morphology of the atomic step templates are determined by the crystal miscut inclination and azimuth, which can be macroscopically defined in the crystal cutting process. These findings open up the possibility of assembling nanotube architectures from the bottom-up by atomic-scale surface engineering. Reference: A. Ismach, L. Segev, E. Wachtel and E. Joselevich, 'Atomic Step-Templated Formation of Single-Wall Carbon Nanotube Patterns', *Angew. Chem. Int. Ed.* **2004**, in press.

2:30 PM GG5.4

Site-selective functionalization of carbon nanotubes.

Raghuveer S Makala, Ashavani Kumar, P. G. Ganesan, G. P. Louie and G. Ramanath; Materials Science & Engineering Department, Rensselaer Polytechnic Institute, Troy, New York.

Functionalizing CNTs with desired moieties, or derivatizing them with other low-dimensional nanostructures, is of widespread interest for applications such as separating CNTs of different chiralities, assembling and interconnecting CNTs, and creating smart composite materials. In order to realize many of these possibilities, it is essential to achieve precise control over the type and location of functionalization. Conventional oxidation routes such as aggressive acid treatments, however, do not allow site-selective functionalization. Here, we demonstrate a completely new approach of using ion-irradiation followed by mild chemical treatments, to site-selectively derivatize preselected segments of CNTs with desired functional groups, nanoparticles, and biomolecules. We use 5-30 keV focused ion beams of Ar⁺ and Ga⁺ to enhance the chemical reactivity of CNT segments by creating defects within a lateral spatial resolution determined by the beam spot size. Desired nanostructures have been selectively attached at the ion-modified segments of the CNTs by electrostatic or covalent interactions. Ion doses in the range of 10¹⁵- 10¹⁷ ions/cm²-depending on the CNT diameter-are the most conducive for defect creation and selective attachment. No observable anchoring is noted at lower doses, compared to unirradiated locations, while higher doses sputter away the CNTs. Air-exposure derivatizes the irradiated CNT segments with allyl, carboxyl, and methyl groups that provide the means for anchoring other nanostructures. For example, we have electrostatically anchored charged gold nanoparticles, and proteins such as azurin and chymotrypsin to carboxyl groups at the irradiated CNT segments. We show that the

anchored proteins retain their bioactivity. Similar approaches can be used to attach DNA site-selectively to CNT segments using the phosphate backbone. We demonstrate covalent attachment by immobilizing carboxylated Nile-red fluorescent nanospheres by displacing Br that decorates allyl groups in the irradiated CNT segments. We show that high-spatial resolution site-selective attachment of nanoparticles and biomolecules on organized arrays of CNTs opens up new possibilities of creating CNT-hybrid chips that could serve as combinatorial laboratories for detecting and separating analytes.

2:45 PM GG5.5

Electrically-Addressable Biological Functionalization of Carbon Nanotubes and Nanofibers. Chang-Soo Lee¹, Sarah E. Baker¹, Matthew S. Marcus², Wensha Yang¹, Mark A. Eriksson² and Robert J. Hamers¹; ¹Chemistry, University of Wisconsin-Madison, Madison, Wisconsin; ²Physics, University of Wisconsin-Madison, Madison, Wisconsin.

One of the major challenges of nanotechnology is the fabrication of high-density biosensor arrays comprised of nanotubes or nanofibers, each modified with distinct biomolecular recognition elements. We have developed a method for electrically-addressable biomolecular functionalization of nanotube and nanofiber electrodes. Using DNA as a prototype, we show that an electrochemical reaction provides a pathway for addressable modification. We verify this by making a small array of distinct DNA oligonucleotides on nanotube electrodes, and show that the resulting DNA-modified nanotubes/nanofibers exhibit excellent selectivity for binding to complementary vs. non-complementary DNA sequences. Furthermore, we demonstrate that the functionalization can be achieved on individual nanofibers and sub-micron fiber bundles without the use of microfluidics. This work provides a practical, inexpensive route toward ultra-high-density, electrically-configurable biosensor arrays.

3:30 PM GG5.6

Spatial Organization of ZnO Nano-Rods on Silver Surfaces. Julia W. P. Hsu, Z. R. Tian, N. C. Simmons, C. M. Matzke, M. A. Rodriguez, J. A. Voigt and Jie Liu; Sandia National Laboratories, Albuquerque, New Mexico.

ZnO is a technologically important material because of its multi-functionalities that range from piezoelectric transducers and varistors to wide-bandgap semiconductor for UV emitters and detectors. In addition to polycrystalline ceramic powders and epitaxial thin films, recent advances in ZnO have been in vapor-liquid-solid growth of nanowires and solution growth of nanorods. For these nanostructures to be useful, a means to place them strategically on the surface is needed. Here we apply micro-contact printing to selectively modify the growth surfaces with patterned self-assembled monolayers (SAMs), which in turn determines the final spatial organization of ZnO nano-rods. Such an approach is purely additive, i.e. depositing materials only where they are desired, and avoids contaminating the pristine surfaces elsewhere. In addition to spatial selectivity, crystal morphology and hierarchical structures can be tuned through solution chemistry and growth conditions. ZnO nano-rods (grown on Ag film substrates) displayed strong c-axis out-of-plane texture when surrounding regions are covered with mercaptoalkanoic acids (HSC_nH_{2n}COOH). We have achieved excellent selectivity with virtually no nano-rods grown on the SAM regions. The mechanism of selectivity will be discussed. The density of nano-rods inside the patterned Ag areas is substantially higher than that of nano-rods grown on unpatterned Ag. Furthermore, we can control the average density with patterns over 2 orders of magnitude! In addition, by tuning the feature size and solution chemistry, we are making progress towards growing isolated individual nano-rods on lattices. 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.

3:45 PM GG5.7

Fabrication of 2D Photonic Crystal Based on Patterned and Aligned ZnO Nanorods. Xudong Wang, Elton Graugnard, Jeff King, Zhong Lin Wang and Christopher J. Summers; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Quasi-one-dimensional (1D) zinc oxide, a direct wide band gap (3.37eV) semiconductor with a large excitation binding energy (60 meV), is one of the most important functional oxide nanostructures, exhibiting near-UV emission, transparent conductivity and piezoelectricity. The growth of patterned and aligned 1D ZnO nanostructures has many potential applications in sensing, optoelectronics and field emission. The aligned growth of ZnO nanorods has been successfully achieved on a solid substrate via a vapor-liquid-solid (VLS) process with the use of gold and tin as catalysts, in which the catalyst initiates and guides the growth, and

the epitaxial orientation relationship between the nanorods and the substrate leads to the aligned growth. By combining the surface epitaxial approach with the self-assembly based mask technique, large-area hexagonally patterned, aligned ZnO nanorod arrays have been fabricated on a single crystal Al₂O₃ substrate. The synthesis process involves three main steps. First, a large-area, self-assembled and ordered monolayer of sub-micron polystyrene (PS) spheres was formed on a single crystal Al₂O₃ substrate. Second, a thin layer of gold was deposited onto the monolayer; and then the spheres were etched away, leaving a patterned gold catalyst array. Finally, nanorods were grown on the substrate using a VLS process. This approach opens the possibility of creating patterned 1D nanostructures for applications such as nano-optic devices, sensor arrays, piezoelectric antenna arrays, and interconnects. Using atomic layer deposition (ALD) technique, TiO₂ layer can be deposited around the surface of all the ZnO nanorods. With the growth of this layer, all of the space between the nanorods can be filled and consequently form a continuous TiO₂ wall, which follows the honeycomb-like pattern. (Conversely, this structure can be viewed as a highly packed air-hole array in a TiO₂ matrix). The dielectric matrix of this 2D photonic crystal is constructed from two different dielectric materials that form "core/shell walls". This type of structure can be a good candidate for a wide-bandgap 2D photonic crystal.

4:00 PM **GG5.8**

Nano-Carpet Effect: The Wetting of Vertically Aligned Si Nanorod Arrays. Yiping Zhao and Jianguo Fan; Physics and Astronomy, University of Georgia, Athens, Georgia.

The wettability of a solid state surface is affected by both the surface roughness and the surface chemical composition. Recent studies have shown that nanoscale structures such as polymer fiber arrays [1, 2] and carbon nanotube arrays [3], treated by proper chemicals, will produce the super-hydrophobic property. However, a systematic study on the effect of nanorod arrays on the wettability is hard to achieve due to the limitations of the fabrication techniques. Here, we report a systematic investigation on the wettability of vertically aligned Si nanorod arrays with different heights (aspect ratio) fabricated by the glancing angle deposition technique. The equilibrium water contact angles of vertical aligned nanorod Si films were measured by the sessile drop method. For as-deposited hydrophilic films, there was a contact angle transition from a rough surface to a hemi-wicking porous surface at normal film thickness $d = 500$ nm; while for the HF treated hydrophobic films, a transition from partial composite to composite surface was observed at the same film thickness. The observed results can be reasonably interpreted within framework of the classic Young's theory. We have also observed that for the hydrophilic nanorod arrays, the spreading of the water droplet deforms the nanorods on the surface, and generates intriguing percolation patterns that change with the spreading diameter. This so-called nano-carpet effect reflects the dynamic spreading process, and from the deformed nanorods, one can estimate the dynamic capillary interaction between the water and the nanorods. Acknowledgement: Work supported by NSF. 1. H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, and D. B. Zhu, *Angewandte Chemie-International Edition* 40, 1743 (2001). 2. L. Feng, S. H. Li, H. J. Li, J. Zhai, Y. L. Song, L. Jiang, and D. B. Zhu, *Angewandte Chemie-International Edition* 41, 1221 (2002). 3. Kenneth K. S. Lau, Jose Bico, Kenneth B. K. Teo, Manish Chhowalla, Gehan A. J. Amaratunga, William I. Milne, Gareth H. McKinley, and Karen K. Gleason, *NanoLetters* 3, 1701 (2003).

4:15 PM **GG5.9**

Synthesis and Applications of Hierarchical Nanowire Networks. Donghai Wang, Rong Kou, Maria P. Gil and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanoscale building blocks, such as quantum dots, nanoparticles, nanorods, nanowires, nanobelts, nanotubes, and nanomesh, have attracted tremendous attention due to their peculiar and fascinating properties. It is necessary to assemble low dimensional nanoscale building blocks into nanostructured systems for the potential applications in energy storage, separation, catalysis, computation, sensing, etc. In this work, we report the synthesis, characterization and applications of macroscopic hierarchical metal or semiconductor (e.g., Pt, CdSe) nanowire networks. These nanowire networks were electrodeposited within the pores of highly-ordered mesoporous silica films followed by removal of the silica template, resulting in robust nanowire networks. With the introduction of silica porogens into the self-assembled mesostructured silica followed by electrodeposition, hierarchical porous nanowire networks have been achieved. The nanowire networks have been characterized using XRD, TEM, SEM, cyclic voltammetry, and other techniques. The nanowire diameter and network microstructure were controlled by the pore size and mesostructure of the silica template. As-synthesized metal nanowires self support to form networks with high electrochemical active surface area, which was further fabricated into glucose sensor through immobilization of enzyme into the Pt nanowires. The enzymatic Pt

nanowire networks show 5-10 times higher sensitivity of glucose detection than the bare Pt electrode based sensor due to the increased active surface areas. The enzymatic Pt nanowire glucose sensors retain its sensitivity for a month, while the sensitivity of bare Pt sensor decreases after 3 days. The Pt nanowire networks with preferred surface crystallographic orientation or isotropic polycrystalline surface properties can be synthesized by controlling the nanowire mesostructures from 2D to 3D. Semiconductor CdSe nanowire networks show tunable absorption peaks in Uv-Vis spectra by controlling nanowire diameter. We have also fabricated 3D CdSe nanowire network/organic heterojunctions showing promising efficiency in photovoltaic. In conclusion, this work provides an easy and efficient way to synthesize macroscopic hierarchical nanowire networks with well-controlled diameter and mesoscale arrangement, which will be of great interest for sensor, photovoltaic, and other applications.

4:30 PM **GG5.10**

Single Crystalline One-Dimensional Structures by Self-Assembly of PbSe Nanocrystals. Dmitri V. Talapin, Kyung-Sang Cho, Charles Black, Robert L. Sandstrom and Christopher B. Murray; T.J. Watson Research Center, IBM, Yorktown Heights, New York.

We report the formation of single crystalline PbSe nanowires via self-assembly of PbSe nanocrystals. The diameter, shape (cross-section) and length of the wires are tailored by controlling the reaction conditions. In this synthesis nearly spherical PbSe nanocrystals are formed and grown in solution until they reach a critical size where attractive forces drive their assembly into wires. Induced dipole-dipole interactions favor formation of long linear chains of PbSe nanoparticles followed by their fusion into undulating, chain-shaped wires. The nanocrystals fuse by oriented attachment with binding (100) facets of individual particles. The formed wires can grow further by consuming lead and selenium precursors from the surrounding solution. This process is affected by the presence of surfactants (primary amines, phosphine oxides, alkyl phosphonic acids, etc.) which can selectively bind to either the lead precursor or the PbSe wire surface. Depending on the growth rates along (100) and (111) crystallographic directions, we observe formation of either long (up to 30 microns) straight wires with diameter adjustable from 3 to 20 nm or branched star-shaped nanowires. The use of various stabilizing agents allows formation of periodic zig-zag nanowires as well as single crystalline PbSe nanorings. By simultaneous control over lateral and longitudinal growth rates, we are able to grow tapered nanowires whose bandgap changes along their length due to the effect of quantum confinement. We propose the technique of aligning PbSe nanowires on-chip by applying an external electric field, thus facilitating their integration into devices. Preliminary electronic measurements demonstrate the potential of solution phase grown PbSe nanowires in FETs and IR active opto-electronic nanodevices.

4:45 PM **GG5.11**

Assembly of Silicon Nanoparticles Roll Up into Flexible Nanotubes. Munir H. Nayfeh¹, Sahraoui Chahel² and Adam Douglas Smith¹; ¹Physics, University of Illinois, Urbana, Illinois; ²Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We report on flexible nanotubes made of a self-assembly of silicon nanoparticles. We showed that when a colloidal dispersion of fluorescent silicon nanoparticles in alcohol is submitted to an electric field, a current is generated and the particles are driven to one of the electrodes via electrophoresis. This method allows us to coat various surfaces with a thin film of silicon particles. Upon drying, the film rolls up into uniform tubes. Using Atomic Force Microscopy (AFM) and a linear elasticity model we were able to measure the Young's modulus of this film. It was found to be as flexible as rubber. These structures constitute the basis for future enhanced biological recognition and sensing of toxins. Moreover, they are useful as catalysts, and in nano robotic applications.

SESSION GG6: Poster Session: Mesoscale Architectures from Nanounits: Assembly, Fabrication and Properties I
Chairs: Paul Braun, G. Ramanath and Mauricio Terrones

Tuesday Evening, November 30, 2004

8:00 PM

Exhibition Hall D (Hynes)

GG6.1

Edge Spreading Lithography: A New Technique for Nanoscale Fabrication. Joseph M. McLellan, Matthias Geissler and Younan Xia; Chemistry, University of Washington, Seattle, Washington.

We have recently demonstrated a simple and convenient method for

developing the outer profile of objects supported on a solid surface. In our initial demonstrations, we formed arrays of silica beads on gold and silver substrates by means of self-assembly, and then printed alkanethiols onto these arrays using a planar PDMS stamp. These arrayed beads served as guides to deliver the alkanethiols to the metal surfaces where they reacted to form self-assembled monolayers. These patterned monolayers could serve as ultra-thin resists in a subsequent selective etching process. When silica beads were used as the guides, ring-type structures were formed due to the circular footprints of the beads. Rings with inner diameters from 0.1-0.7 μm and ring widths from less than 100 nm to greater than 1.0 μm could be generated by varying parameters such as the diameter of the silica beads, the concentration of thiol, and the contact time of the stamp. This talk will focus on the experimental procedures, capabilities, and limitations associated with this technique. I will also discuss the use of guides other than silica beads, as well as the extension of this technique to smaller scales.

GG6.2

Microcontact Printing and Molding of Nanocrystal Thin Films. LeeAnn Kim¹, Seth Coe-Sullivan¹, Jonathan S. Steckel², Mounqi G. Bawendi² and Vladimir Bulovic¹; ¹Laboratory of Organic Optics and Electronics, MIT, Cambridge, Massachusetts; ²Department of Chemistry, MIT, Cambridge, Massachusetts.

Creating active devices from nanometer sized components requires the precise placement of materials in all three dimensions. Colloidally grown quantum dots are typically deposited from solution, using techniques such as spincoating and dropcasting. These solution based processes limit the types of substrates on which deposition can be performed and do not provide for controllable in-plane patterning. These shortcomings have to date been the primary barrier to the creation of high performance devices utilizing such nanomaterials. By extending the methods of microcontact printing and molding to nanocrystal deposition, we have overcome these obstacles. We demonstrate two dimensional patterned deposition of quantum dots onto diverse substrates, such as silicon, metals, and amorphous organics. This deposition technique has been utilized for the fabrication of bright, highly efficient, and color saturated quantum dot light emitting devices.

GG6.3

Novel Technique for Preparation of Dipolar Microparticles by Polymerization of Polarised Emulsions. Vesselin N. Paunov¹, Olivier J. Cayre¹, Hartmut A. Wege¹ and Orlin D. Velev²; ¹Department of Chemistry, University of Hull, Hull, United Kingdom; ²Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

We have developed a novel method for fabrication of dipolar colloid particles, which is based on polymerisation of oil-in-water emulsions stabilised with a mixture of water-insoluble cationic and anionic surfactants. An emulsion of polymerisable oil in water is polarized in DC electric field which causes segregation of the positive and the negative surface charges (coming from the cationic and anionic surfactant) on the surface the emulsion droplets. We polymerize the emulsion drops while the surfactants adsorbed on their surfaces are polarized in order to 'freeze' the dipolar surface charge distribution. Thus, we produce a suspension of polymer microparticles of permanent electric dipolar moment. Successful polarization of the surface charges on the particles has been visualized by fluorescence microscopy by using two fluorescent surfactants of opposite charge. Our results show that the produced polymer microparticles retain their polarisation when the electric field is switched off for at least several months. Without polymerisation, the emulsion drops quickly relax to uniform surface distribution of the cationic and the anionic surfactant. The use of this method has been extended to core-shell colloids by coating colloidal particles with the polymerisable oil and using the same mixture of surfactants. This has been done with spherical melamine resin particles and polymer microrods. The proposed simple method for bulk preparation of dipolar colloids allows easy up-scaling to industrial production. Possible applications of these dipolar colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids.

GG6.4

Anisotropically Etched Silicon Masters for Nanofabrication. Albert M. Hung¹ and Samuel I. Stupp^{1,2,3}; ¹Materials Science and Engineering, Northwestern University, Evanston, Illinois; ²Chemistry, Northwestern University, Evanston, Illinois; ³Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

The simple, functional patterning of self-assembling nanostructures on surfaces is a problem of interest in our laboratory. For this purpose we have demonstrated the feasibility of using anisotropically etched silicon as a master mold for generating sub-micron features by a

variety of lithographic techniques. The approach involves the use of conventional photolithography and subsequent wet etching of (100) silicon in KOH solution to produce a faceted surface structure with [110] ridges as thin as 20nm at the apex. This rigid mold was used to emboss features down to 100nm in a polymethylmethacrylate (PMMA) thin film by nanoimprint lithography. Replicas of the mold in polydimethylsiloxane (PDMS) or polyurethane allowed for better conformal contact with the substrate, and a voltage applied between a gold-coated stamp and a silanized silicon substrate resulted in electrically assisted chemical patterning of the silane layer with sub-micron resolution. The molds could also be used for micro-contact printing of self-assembled monolayers or patterned electrochemical deposition. This bench-top method could be attractive as a highly versatile way of fabricating complex nanopatterns over a large area without the need for an expensive master.

GG6.5

Guided Assembly of Nanoparticles using Nanotemplates. Ahmed A. Busnaina, Xiong Xugang and Jason Small; Nanomanufacturing Research Inst., Northeastern University, Boston, Massachusetts.

Current nanotechnology research focuses on surface modification, matching molecules and "sockets" at the level of manipulating several to several hundred particles or molecules to be assembled into desirable configurations. Commercial scale-up and the promised economic windfall, however, will not be realized unless one can perform high-rate/high-volume assembly of nanoelements economically. Nanotemplates will enable high-rate/high-volume bottom-up, precise, parallel assembly of nanoelements (such as nanoparticles, carbon nanotubes, nanorods, and proteins) and polymer nanostructures. The proposed nanotemplates and processes will accelerate the creation of highly anticipated commercial products and will enable the creation of an entirely new generation of applications. Although self-assembly of nanoelements may produce uniform patterns or structures, such patterns are difficult to control and manipulate to produce specific design or structures. The proposed nanotemplates, however, will act as platforms or tooling to force the self-assembling of nanoelements into consistent patterns. Some of these nanotemplates can be used as manufactured, but most must be functionalized for ultimate use in nanomanufacturing processes. The Nanopatterns used in the templates can be manufactured using e-beam, dip pen, and nanoimprint lithography. The electrostatically addressable nanotemplate offers a simple means for controlling the placement and positioning of nanoelements through conductive nanowires. The nanowires can be manufactured in different patterns and designs using nanolithographic techniques or other self-assembly techniques. Although microchannels and electric fields have been for local assembly of carbon nanotubes for interconnects and electromechanical probes have been explored, these techniques do not provide precise large-scale assembly at high rates and high volumes. The nanoparticles or nanotubes align on the charged wires of the nanotemplate. The nanotemplate and nanoelements can form a device or can function as a template to transfer patterned arrays of nanoelements onto another substrate. When the nanotemplates are moved with nano-precision accuracy and alignment, they can be used to deposit a wide variety of nanoelements into very closely packed columns or rows with a very narrow pitch. Preliminary results show the use of nanotemplating nanowires in the guided self assembly of nanoparticles along a 60 nm nanotemplate's gold nanowires. Using red fluorescent particles show that PSL particles are attracted to positively charged wires only. Techniques have also been developed to prevent or remove any nanoparticles that may deposit anywhere else (other than on the positively charged nanowires).

GG6.6

Nano-patterning of Multiple Self-assembled Monolayers for Bio-MEMS. Jang Gil Kim, Vincent Blech, Nobuyuki Takama and Beomjoon Kim; Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Nowadays, with increased demands for nano scale patterning technique, micro contact printing (μCP) has gained much interest as master & replication techniques for its great versatility, high throughput and potentially low cost [1]. However, despite these numerous advantages, difficulties remain in μCP for nano scale patterning. The fabrication of nano scale master of the stamp requires expensive and complicated process such as EB-lithography. In addition, Sylgard 184 (Shore A hardness, 50), the most commonly used material for fabricating the stamp, enables conformal contact with the substrate due to low hardness, but it is easily deformed and, therefore, leads to collapse effect. Alternative solutions such as composite stamp have been proposed in order to overcome this problem [2], [3]. To make more precise pattern on nano scale with low cost, we studied two methods: the use of micrometer scale pyramidal stamp and a novel hard PDMS. KOH anisotropic etching of Si substrate was used to obtain pyramidal (or V-shaped) grooves, with

typical width of 4 μm . From such master, a PDMS stamp with sharp tip pyramidal relief was molded, allowing the replication of nano-scale dot patterns of SAM (hexadecanethiol) by μCP . However, the deformation and collapse of the stamp still remains as a concern. In order to reduce this effect and, therefore, take advantage of the pyramidal shaped stamp, not only the force on the stamp can be controlled, but also the hardness of the stamp. We used novel type of hard PDMS (Shore A hardness, 79) which allowed reaching 500 nm dot patterns with very simple and inexpensive process. Stamps with pyramidal tips or V-shaped grooves then allow reaching the nanoscale, whereas the original photomask is microscale. Two stamps of this kind have been used in a second process, consisting in patterning three different types of molecules self-assembled on the surface of the same substrate. This allows local, selective attachment of biomolecules for bio-sensor applications. References [1] B. Michel et al., IBM J. Res. & Dev. Vol. 45 No. 5 Sep 2001 and references therein... [2] H. Schmid, B. Michel, *Macromolecules* 33, pp. 3042-9 (2000) [3] T.W. Odom, J.C. Love, D.B. Wolfe, K.E. Paul, and G.M. Whitesides, *Langmuir* 18, pp. 5314-20 (2002)

GG6.7

Focused Ion Beam Patterning of Transparent Oxide Substrates for Epitaxial Assembly of Colloidal Crystals. Summer K. Rhodes¹, Jennifer A. Lewis^{1,2,4}, Paul V. Braun^{1,3,4} and Ryan J. Kershner^{1,4}, ¹Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois; ²Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois; ³Micro and Nanotechnology Lab, University of Illinois Urbana-Champaign, Urbana, Illinois; ⁴Beckman Institute for Advanced Science and Technology, University of Illinois Urbana-Champaign, Urbana, Illinois.

Direct writing with a focused ion beam (FIB) was used to generate 2-D square arrays of dimpled features in transparent oxide substrates. These periodic patterns were created with well-controlled hole diameter and depth at a pitch of 500 nm (colloid diameter) to guide the epitaxial assembly of colloidal crystals. In the absence of precise FIB calibration, large variations between the targeted and actual pitch (500 \pm 100 nm) were observed for the patterns generated. This degree of control is not suitable for colloidal templating, since size variations of less than 5% of the colloid diameter are required for crystallization. Through an iterative FIB calibration involving the use of an internal standard, the pattern reproducibility was improved by an order of magnitude, such that a substrate pitch of 500 \pm 10 nm was achieved. The effects of ion beam current, beam dwell time, and total milling time on the resulting patterned features were systematically studied. Atomic force microscopy (AFM) was carried out on as-patterned and etched substrates to quantify their uniformity and characteristic feature sizes. By etching, we can generate smooth, enlarged dimpled features free of remnant debris produced during the milling process. Experiments are now underway to explore the epitaxial assembly of colloidal microspheres during gravity-driven sedimentation on these patterned substrates.

GG6.8

Site-selective integration of monolayer-protected metal nanoparticles on two-dimensional organic surface templates. Kensuke Akamatsu¹, Jun Hasegawa¹, Hidemi Nawafune¹, Nagahiro Saito² and Osamu Takai², ¹Konan University, Kobe, Japan; ²Nagoya University, Nagoya, Japan.

Composite micro- and nano-structures consisting of metal nanoparticles and organic surroundings have recently attracted much attention for both fundamental and practical reasons. In particular, much effort has been devoted to directing monolayer-protected metal nanoparticles into organized structures onto solid supports by a variety of fabrication techniques. One of the emerging techniques for immobilization is to use organic monolayers attached on the nanoparticles and substrate of interest to guide the assembly of the nanoparticles through pre-designed chemical and physical interactions. In this study, we demonstrate a novel technique for the fabrication of two-dimensional microscopic assembly of monolayer-protected gold nanoparticles onto substrates. The surface properties of carboxylic acid monolayers attached on gold nanoparticles were used to guide the site-selective deposition of the nanoparticles onto organic monolayer templates prefabricated on glass substrates. In this approach the gold nanoparticle assemblies were deposited and integrated as two-dimensional microscopic circuit patterns through the process of simple coating of the solution containing gold nanoparticles and drying followed by solvent-induced lift off. Selective integration of the nanoparticles onto either hydrophobic or hydrophilic region on the substrates could be achieved by controlling initial pH of the solution and by selection of the solvents used for lift off process, thereby providing effective methodology for fabrication of both positive and negative patterns of integrated mesoscopic nanoparticle assemblies.

GG6.9

Monolayer and Pattern Formation using Colloidal Particles through Self Assembly. Bratindranath Mukherjee, Shwetha A. Shetty and Ravishankar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Self Assembled monolayer of colloidal particles find applications in diverse fields such as photonic band gap crystals, physical lithographic mask and diffractive elements for optical sensors. In the present work, monolayers of latex spheres of different sizes ranging from 50 nm -1.6 micron on different plane/patterned substrates have been prepared. Issues relating to the effect of surface charge, concentration of colloidal dispersion, physical nature of the substrate (hydrophilic/hydrophobic) and anisotropy of the substrate on monolayer/pattern formation have been investigated in detail. This leads to useful insight in to the process of self assembly and is helpful to control such colloidal layers and crystals.

GG6.10

Preferential patterning of metal oxides on metal oxide-recognizing peptides - Selective patterning of zinc oxide and europium oxide particles- Mitsuo Umetsu¹, Masamichi Mizuta¹, Satoshi Ohara¹, Seiichi Takami¹, Hideki Watanabe², Kouhei Tsumoto², Izumi Kumagai² and Tadafumi Adschiri¹, ¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; ²Biomolecular Engineering, Tohoku University, Sendai, Japan.

Recent advances in nanotechnology have enabled us to utilize responses of nanocluster to electron, magnetic and photo fields. The application of nanocluster to a photo/electron device has been attempted, but a new patterning technique apt for nano particle is required. Zinc oxide (ZnO) is one of the most widely used semiconducting oxides for electronical, magnetic and optical applications, so that the nano-structuring of ZnO has become a focus of considerable attention. In this study, we select a peptide with the affinity for ZnO from a phage-display library, and assembly fluorescent ZnO particles on gold plane with the ZnO-recognizing peptide. The phage library with a 12-mer peptide on the surface (Ph.D.-12 Phage Display Peptide Library Kit, New England Biolab) was applied for selection of a peptide sequence with the affinity for ZnO. The three-time panning procedures resulted in the observation that 24 of 48 phages have the identical displayed peptide sequence. The selected peptide was organically synthesized with a cysteine residue at the C-terminus, and then it was immobilized on an Au film through an Au-S linkage. The peptide-immobilized Au film was soaked in a fluorescent ZnO suspension and washed several times by a detergent solution for excluding non-specifically-binding ZnO particles. In comparison to an Au film without the ZnO-recognizing peptides, the peptide-immobilized Au film showed an intense fluorescence derived from ZnO. It should be noted that the ZnO-recognizing peptide showed no specificity for europium oxide and zinc sulfide particles. We would show the peptides with the affinity for europium oxide and other metal oxides.

GG6.11

A Mesoscale Template Prepared by the Self Assembly of Synthetic Polypeptide. Honggang Cu¹, Jeffery Thompson², Timothy J. Deming² and Darrin J. Pochan¹, ¹Department of Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware, Newark, Delaware; ²Department of Materials and Chemistry, University of California at Santa Barbara, Santa Barbara, California.

Control of the detailed structure of matter on many length scales is a major goal of chemistry, materials science and nanotechnology. The structure and function of synthetic polypeptide single crystal surfaces may provide a useful base to template material growth from the nanoscale to microscale level. Single crystals of synthetic poly(L-lysine) (PLL) polypeptides have been grown up to many microns in diameter from aqueous solution by the addition of salts or nonsolvents. Circular dichroism (CD) data showed that the crystal structure was defined on the nanoscale by the alpha helical secondary structure of PLL chains in the mother solution, which can be controlled by either PH or temperature. The resultant single crystals morphologies were studied by transmission electron microscopy (TEM), atomic force microscopy (AFM), and field emission scanning electron microscopy (FESEM). PLL single crystals exhibited the forms of regular hexagonal lamellae in both monolayer and multilayer forms with or without a central screw dislocation depending on the growing conditions. The thickness of the resultant crystals can be directly controlled by the PLL molecular weight. The local hexagonal lattice structures of single crystals both in solution and in film were obtained by X-ray scattering and electron diffraction. The application of polypeptide single crystals as templates to control the crystallization of minerals and the assembly of metal nanoparticles was initially investigated.

GG6.12

Fabrication of Highly Ordered Anodic Porous Alumina using a Self-Organized Particle Array. Yoshitaka Matsui¹, Futoshi Matsumoto¹, Kazuyuki Nishio^{2,1} and Hideki Masuda^{2,1}, ¹Kanagawa Academy of Science and Technology, Kanagawa, Japan; ²Tokyo Metropolitan University, Tokyo, Japan.

Highly ordered anodic porous alumina, which has a fine channel structure with uniform-sized holes of nanometer scale and high aspect ratios, has recently attracted much interest as a starting material for the fabrication of several kinds of nanodevices. We have reported that an ideally ordered single domain hole array structure with uniform, straight channels and ideal hexagonal arrangement could be obtained by adding anodization of Al to the pretexturing process of Al with a master for generating the array of concaves on the surface of Al substrate.[1] The array of concaves initiates the development of pores. However, the master used was a SiC mold prepared using expensive electron-beam lithography and ion-etching apparatuses. In the present work, we show a new preparation of anodic porous alumina with highly ordered submicron-sized channels by means of a polystyrene particle array formed by self-organization of the particles as a master.[2] Two-dimensional ordered array of polystyrene particles with 200 nm in diameter was fabricated on the glass plate by slowly evaporating the water solvent in which polystyrene particles were dispersed. An Al layer was deposited on the two-dimensional ordered particle array by vapor deposition. The polystyrene particles were removed from the deposited Al by immersing the Al substrate into toluene. Anodization of the Al substrate was carried out at a constant voltage. The fabrication of an ideally arranged hexagonal cell configuration having a cell size of 200 nm which corresponds to that of the pretextured concaves on the surface of deposited Al was confirmed. This result demonstrates the feasibility of employing self-organized particle array as a master for the fabrication of long-range-ordered channel array architecture. [1] H. Masuda et al., *Appl. Phys. Lett.*, 71, 2770 (1997). [2] H. Masuda et al., *Chem. Lett.*, 33, 584 (2004).

GG6.13

Self-Assembled Mesoscale Hollow Capsule Reactor for Unusual Material Synthesis. Won San Choi, Jeong-Ho Park, Hye Young Koo, Seung Hwan Oh and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Recently, a new concept of chemical synthesis of organic/inorganic materials inside or surface of polyelectrolyte hollow capsules was introduced. However, most of these include the synthesis of nanosized magnetite or organic materials. As far as polymerization reaction is concerned, there are only a limited number of reports. We have investigated the difference of polymerization reaction between inside and outside of hollow capsules having confined geometry. A water soluble initiator bound hollow capsules were used as a nanoreactor. After polymerization, the shape of capsules could be manipulated by monomer contents. The polymers grown from the inner surface of capsules had an order of magnitude higher molecular weight than the polymers grown from inside as well as the polymers grown from outside. This polymerization behavior could be further controlled by the capsule size and monomer contents.

GG6.14

Colloidal Clusters of Silica or Polymer Microspheres. Gi-Ra Yi^{1,2,3}, Vinothan N. Manoharan², Seung-Man Yang³, David J. Pine² and Seung-Kon Lee³, ¹Corporate R&D Center, LG Chem Co., Daejeon, South Korea; ²Department of Chemical Engineering, University of California, Santa Barbara, California; ³Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

We demonstrate an emulsion encapsulation and shrinkage technique for producing large quantities of colloidal stable clusters of hydrophobic microspheres, including sterically stabilized silica, poly(methyl methacrylate), and polystyrene particles. We find that the sequence of cluster structures is identical for the three systems when the number of spheres in a cluster (n) is less than 11. Despite the differences in particle properties and interactions in the various systems, the sequence of structures remains remarkably consistent even at larger n , suggesting that the sphere packing process may work for a wide range of colloidal materials. The flexible and robust process can be used to prepare clusters with shapes such as doublets, tetrahedra, icosahedra, and others, all of which can be rendered colloidal stable in either oil or water through a simple silica coating technique.

GG6.15

Fabrication of Tailor-made Substrates for Self-assembly of Protein Molecules. Chi Won Ahn and Henny W. Zandbergen; Kavli Institute of Nanoscience Delft, Delft University of Technology, Delft,

Netherlands.

Information of a protein's structure is essential for the understanding of its function. Protein crystallization to obtain crystals large enough for X-ray diffraction is often the bottleneck in the structure determination process. We investigate two routes to by-pass this problem: the use of electron diffraction since electron diffraction requires much smaller crystals (typically 10^6 times smaller) and the use of tailor-made substrates to enhance the initial crystallization. Concerning the latter, we have applied nanotechnologies ("bottom-up" and "top-down" process) to fabricate tailor-made substrates for self-assembly of protein molecules. As top-down processes, optical, electron beam, and focused ion beam lithography methods are used to make nano-patterned a-SN (amorphous-Silicon Nitride) substrates. These a-SN membranes are used for a substrate to put on protein molecules by "bottom-up" process as like a self-assembly process. We will discuss the preparation and characterization of the tailor-made substrates and their effectiveness in the assembly of protein molecules.

GG6.16

Nanostructured Nanoparticles: A Novel Material to Prevent Protein Non-Specific Adsorption. Alicia M. Jackson and Francesco Stellacci; Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Recently, we have developed a new class of nanomaterials.[1] These are monolayer protected metal nanoparticles coated with a mixture of ligands that spontaneously forms sub-nanometer phase separated domains. In the case of two ligands, in which one is hydrophobic and the other is hydrophilic, ring of alternating composition form and encircle the nanoparticle metallic core. The 'footprint' of each hydrophobic or hydrophilic region is no more the 6 \AA wide. Proteins are known to nonspecifically adsorb on surfaces by a mechanism that involves conformational changes and maximization of the attractive van derWaals and electrostatic forces between the material surface and the protein's exterior. This type of mechanism is inhibited in the case of protein adsorption on surfaces evenly coated with hydrophobic/hydrophilic nanostructured nanoparticles. In fact, each domain on the particle's shell is as small as a single amino-acid, thus the protein is not solely attracted or repelled to such surfaces. As a consequence the net interaction force between the protein and the surface is smaller than the solvation energy and proteins tend to stay in solution. Here we will present a series of measurements that aims at the systematic understanding of the intra-molecular interactions between proteins and nanostructured nanoparticles. In particular, quantitative comparisons (made using FTIR, XPS and fluorescence microscopy) between the protein resistance of surfaces coated with these particles and surfaces coated with industrial standards, such as poly-ethylene-glycols, will be presented. High Resolution Force Microscopy (HRFS) results coupled with theoretical models have been used to elucidate the protein structure and the molecular nature of the interactions between the ligand shell nanodomains and the proteins. The main results will be presented. Also, preliminary results in decoupling the solvation effects from the intra-molecular effects will be discussed. 1 A. Jackson, J. Myerson, and F. Stellacci, *Nature Materials* 2004, 330

GG6.17

Two-Dimensional DNA-directed Assembly of Colloids into Defined Arrays. Margaret H.S. Shyr^{1,2}, Robert A. Barry^{1,2}, Pierre Wiltzius^{2,1} and Paul V. Braun^{1,2}, ¹Materials Science & Eng., University of Illinois Urbana-Champaign, Urbana, Illinois; ²Beckman Institute, Urbana, Illinois.

DNA-derivatized polystyrene nanoparticles were assembled onto DNA-functionalized surfaces in spatially-defined two-dimensional structures by exploiting highly specific Watson-Crick binding interactions that occur between complementary single-stranded DNA. Using microcontact printing, a glass substrate was patterned with ssDNA. Polystyrene colloids were functionalized with complementary ssDNA. Via hybridization of the matching sequences, we were able to direct the colloidal assembly onto the substrate into a variety of patterns, including periodic structures, which were studied through simple laser diffraction. Fluorescence microscopy confirmed that assembly did indeed occur through complementary DNA binding and not through nonspecific interactions: colloidal particles functionalized with non-complementary ssDNA did not bind to the surface. High resolution imaging of the two-dimensional colloidal assemblies was done using SEM. Finally, as DNA interactions are temperature sensitive, we have investigated the response of the colloidal assemblage to thermal annealing.

GG6.18

Self-Assembly of Genetically Engineered Molecular Interconnects. Natalya I. Topilina¹, Seiichiro Higashiya¹, Vladimir V. Ermolenkov¹, Christopher C. Wells¹, Christopher Kossow², Narendra Rana², Eric T. Eisenbraun², Alain E. Kaloyeros², Robert E.

Geer², Igor K. Lednev¹ and John T. Welch¹; ¹Department of Chemistry, University at Albany-SUNY, Albany, New York; ²College of Nanoscale Science and Engineering, University at Albany-SUNY, Albany, New York.

Physico-chemical effects such as pH, ionic strength, and temperature, on self-assembly of bioengineered, β -sheet forming repetitive polypeptides for application to nanoscale building blocks, templates, and device construction were studied by various methods including surface probe microscopy and novel deep UV Raman spectroscopy. The different factors that modulate the folding of repetitive polypeptides to the secondary, tertiary, and quaternary structures, and the monomers to the mesoscopic fibrils by intermolecular assembly are discussed. The repetitive and block-copolymerized β -sheet forming polypeptides have been prepared by a generalized strategy for libraries of artificial repetitive DNA sequences that were prepared based on unidirectional head-to-tail polymerization. The DNA oligomerization/block copolymerization was performed in the presence of adapters containing appropriate recognition sites of a type II restriction endonuclease for regeneration of assembled DNA units with non-palindromic cohesive ends. Repetitive coding sequences were successfully constructed in a reproducible and predictive manner without the need for special cloning vectors while suppressing the intramolecular cyclization of multimers that is problematic when longer sequences are constructed. Several amphiphilic repetitive polypeptides were designed, coded, and constructed. Constructed DNAs were expressed in standard and commercially available *E. coli* expression systems. Results for several key peptides are discussed focusing on those structures with customized length and functionality. The physico-chemical properties of these materials are also discussed within the context of a convenient concentration-based method for separation of fibrils and monomers.

GG6.19

Controllable Growth of Nanowire Arrays in One Dimensional Solid-State Nanoreactors. Andrei Anatolevich Eliseev¹, Kirill Sergeevich Napolskii¹, Irina Valerievna Kolesnik¹, Alexey Viktorovich Lukashin¹, Yuri Dmitrievich Tretyakov¹ and Peter Goernert²; ¹Department of Materials Science, Moscow State University, Moscow, Russian Federation; ²INNOVENT e.V., Jena, Germany.

One of the most important challenges in materials science today is the preparation of nanostructures with the controlled properties and dimensions as well as creation of functional nanomaterials. The most challenging nanosystems are one-dimensional particles or nanowires owing to highest anisotropy parameters in them, which could certainly increase functional properties of nanomaterials. However, the use of the nanostructures as materials is strongly restricted because of their low stability. The approach to this problem is the preparation of the so-called nanocomposite materials. This enables one to avoid aggregation of nanoparticles and protect them from external influences, which simplifies application of such materials. Thus, the main goal of this work is considered as elaboration of basic principles for preparation of nanoparticles with controlled physical properties in one-dimensional solid state nanoreactors (such as mesoporous silica, mesoporous aluminosilicates, anodic alumina, etc). The study represents the formation of magnetic, semiconductor and catalytic nanocomposites based on the metallic (Fe, Ni, Ag, Pt, Fe-Co, Fe-Pt alloys, etc) and metal oxide (α -Fe₂O₃, γ -Fe₂O₃, Fe₃O₄, etc) nanowires grown in one-dimensional solid-state nanoreactors. Nanocomposites were characterized by chemical analysis, HRTEM, ED, SEM, SAXS, SANS and magnetic measurements and optical spectroscopy. It was showed that particles shape and size are in good agreement with the shape and size of the pores in 1D nanoreactors, while the average length of nanowires could be varied in a wide range. Particles are uniform and well ordered in the matrices. Thus, our approach leads to functional materials with nanosized active elements in the matrices, which could find an application in various fields of engineering and technology. This work is supported by RFBR (03-03-32182) and INTAS (01-204).

GG6.20

Nanotube characterization through radial distribution functions: a possible way to determine tube chirality using neutron diffraction. Pedro Armando Ojeda¹, Darin Hoffman², Mauricio Terrones¹, Humberto Terrones¹, Thomas Proffen² and Anthony Cheetham³; ¹Materiales Avanzados, Instituto Potosino de Investigacion Cientifica y Tecnologica, San Luis Potosi, San Luis Potosi, Mexico; ²Research Intern, NPDF, Lujan Neutron Scattering Center, Los Alamos, New Mexico; ³Materials Research Laboratory, University of California, Santa Barbara, Los Alamos, California.

The reduced radial distribution function $G(r)$ of different types of nanotubes (different diameters and chiralities) has been calculated. We find that the $G(r)$ could be used to distinguish arm-chair, zig-zag and chiral nanotubes. Trigonal arrangements of arm-chair nanotubes with different diameters possess characteristic features. In the case of

zig-zag nanotubes, the $G(r)$ signals also exhibit typical patterns that make them recognizable. Experimental $G(r)$ s, obtained from neutron scattering of single walled carbon nanotube samples, are in agreement with the calculated $G(r)$ s of arm-chair nanotubes with diameters ranging from 10 Angs. to 14 Angs. Certainly, chiralities around these arm-chair cases cannot be excluded. The analysis of the zig-zag nanotube bundles is also discussed.

GG6.21

Selective Growth, Diameter Control, and Mechanistic Study of Copper Oxide Nanowires Grown from Exposed Edge of Al₂O₃/Cu/Al₂O₃ Thin Film Multilayer Structure. Nitin Chopra and Bruce Jackson Hinds; Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky.

High aspect ratio and rigid structure of oxide nanowires (NWs) make them useful for nanoscale circuits, interconnects, NEMs, and sensing. For such applications selective growth and diameter control of NWs is crucial. There are several literature examples of CuO NWs being grown by methods as simple as heating Cu foils in air. Our research focuses on diameter control of CuO NWs on patterned silicon substrate by using the dimensional control of narrow lines of Cu (40-100nm) formed at the cleaved/etched face of a Al₂O₃/Cu/Al₂O₃ multilayer structure. Such thin film patterning eliminates the necessity for e-beam lithography as the film thickness determines nm-scale line dimension. The NWs were characterized by SEM, TEM, and EDS studies. NWs were observed to grow only from the 'mesa' structure with average diameter of 39.7, 49, and 88.6 nm were observed for Cu line width of 40, 60, and 100 nm respectively when heated in air at 400C. Standard deviations are 6.4, 6.3, and 26.3 nm respectively indicating larger line widths allow larger deviation in nucleation sizes. The NWs grow with tip diameter smaller than base diameter with an aspect ratio as high as 9, 6, 12 for Cu line width of 40, 60, 100nm respectively. The TEM study of CuO NWs grown from 40 nm thick Cu film (on a Si₃N₄ membrane TEM window as a substrate) at 400°C showed presence of defects/dislocations at the base of NWs indicative role of metal film defects in nanowire growth. The minimal thickness of Cu film for NW growth is about 150 nm at growth temperatures of 500°C and 600°C. This minimum thickness is reduced to 40 nm at 400°C. EDS study shows NW composition as CuO_x ($x = 1.2-1.4$). CuO NWs grown at 400°C have diameters that are determined by Cu line width in multilayer thin film structures. This can be the basis for the directed growth of multidimensional mesostructures of CuO NWs based common thin film fabrication technology.

GG6.22

Electrochemical Fabrication of Mesostructured Metal Nanotubes from Lyotropic Liquid Crystalline Phases. Hongmei Luo, Donghai Wang and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

The discovery of carbon nanotubes in 1991 has initiated intense interest in synthesizing different kinds of tubular structure materials. For example, the metal nanotubes can be prepared by templating synthesis, such as electrochemical deposition of metal in the pores of the template membranes either by using pulse voltage electrodeposition for short time results in nanotube with only 2 μ m length, or by using an organosilane as the molecular anchor to modify the pore-wall of the template. Lyotropic liquid crystalline phases formed at high concentrations of non-ionic polyoxyethylene surfactants can be utilized as versatile nanoscale molds for the formation of highly ordered hexagonal mesoporous metal or semiconductor films. In this work, we extend this technique to electrodeposit crystalline nickel and cobalt nanotubes in porous anodic aluminum oxide (AAO) membranes from lamellar lyotropic liquid crystalline phases. The liquid crystalline templates are characterized by low-angle X-ray diffraction (XRD) and polarized-light optical microscopy (POM). The nanotubes are characterized by wide-angle XRD, field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The obtained crystalline nickel and cobalt nanotubes exhibit ordered mesoscale lamellar structure. The length of nanotubes is easily controlled from several hundred nanometers to tens micrometers by electrodeposition time and the maximum length is the thickness of the template membrane. The magnetic properties of 200 nm sized nickel tubes exhibit anisotropy and coercivity of about 100-120 Oe, comparable to nanowires, higher than nickel film.

GG6.23

Fabrication of Triangular Lattice Arrays of Nano-Dots and Aligned Carbon Nanotubes. Yang Wang, J. Rybczynski, Dezhi Wang, K. Kempa and Z. F. Ren; Physics, Boston College, Chestnut Hill, Massachusetts.

A two-step masking approach has been invented utilizing self-assembly of polystyrene nanospheres to prepare triangular lattice arrays of nano-dots at low cost. A monolayer of self-assembled nanospheres were used as the first mask to construct a secondary mask by

sputtering Ni onto the spheres. This secondary mask was immediately used to pattern triangular lattice arrays of nano-dots. Aligned carbon nanotubes with triangular lattice pattern were grown for the first time from the periodic Ni dots so prepared. Another two-step technique was also invented soon after to successfully obtain triangular lattice arrays of nano-dots as well as aligned carbon nanotubes in a very large scale. The procedure is also applicable to a variety of nano-dot materials on any flat substrates for different application purposes.

GG6.24

Large-Scale Periodic Nanotubes and Nanowires Arrays - Their Fabrication, Modifications, and Properties.

Jakub Ryzczynski, Yang Wang, Debasish Banerjee, Dezhai Wang, Krzysztof Kempa and Zhifeng Ren; Physics Dept., Boston College, Chestnut Hill, Massachusetts.

Self-assembly process of polymer microspheres has been proven as a very simple and cost-effective technique for preparation of large-scale particle arrays. These can be used for a catalytic growth of aligned nanotubes or nanowires with controlled periodicity. The separation of individual nanotubes/nanowires and their arrangement can be modified by the use of different diameter microspheres, mask heating, a double masks use, or further annealing of catalytic nanoparticles. Due to their long-range periodicity these lattices may exhibit interesting optical properties such as photonic bandgap behavior, antenna effect, or lasing action. Recent results of nanotubes and nanowires arrays preparation, modifications, and their optical properties investigations will be presented.

GG6.25

Branched and Hyper-branched Nanowire Structures as Building Blocks for Nanoelectronics and Nanophotonics.

Fang Qian¹, Deli Wang¹, Chen Yang¹, Zhaohui Zhong¹ and Charles M. Lieber^{1,2}; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Branched and hyper-branched silicon nanowire structures were produced via a multi-step nanocluster-mediated synthesis using chemical vapor deposition. Scanning electron microscopy studies confirmed the formation of branched nanostructures and moreover showed that the density of nano-branching can be controlled in a predictable manner. This same approach was also used to grow branched gallium nitride nanowires. High-resolution transmission electron microscopy studies revealed that single-crystal nanowires grew epitaxially from backbone, e.g. silicon nanowires with growth direction of $\langle -11-1 \rangle$ branch out from silicon nanowires with growth axis of $\langle -111 \rangle$. Multiple generations of nanowire branches were grown epitaxially from nanowire backbones with well-controlled composition/doping, and specifically individual silicon-based n-type/p-type branched structures were demonstrated to function as well-defined p-n diodes and junction field-effect transistors. The ability of sequential multi-branching opens up new opportunities for both fundamental studies and nanoscale materials/devices application, including three-dimensional nanoelectronics.

GG6.26

Anodized Aluminum Templates for Nanowire and Carbon Nanotube Field-Effect Transistors. Travis L. Wade¹, Jean-Eric Wegrowe¹, Jean-Francois Dayen¹, Fahd Huwimel¹, Quang Anh¹, Cristina Ciornei¹, Jean-Marie Padovani², Morral Fontcuberta i Anna² and Didier Pribat²; ¹Laboratoires des Solides Irradies, ECOLE Polytechnique, Palaiseau, France; ²Laboratoire de Physique des Interfaces et des Couches Minces, ECOLE Polytechnique, Palaiseau, France.

Anodized aluminum forms a self-assembled, triangular network of nanometer diameter pores that are used as templates for nanostructure synthesis. This is because the pore diameter, distribution, and length can be tailored to suit the needs of the user by varying the anodization conditions: electrolyte, voltage, time, and temperature. The chosen pore size determines the resulting nanostructure dimensions. Another reason is that once the nanostructures have been made in the aluminum oxide template they can be electrically contacted at the top and bottom of the membrane for physical measurements without the need for lithography. With two contacts a scientist can study many interesting phenomena such as magnetoresistance and electron transport in nanostructures. Two contacts, however, is not enough if one wants to make a device such as a transistor for applications or research. A third contact or electrode is needed. An aspect of our research is the development of templates that allow placement of a third electrode close enough to the nanowires or carbon nanotubes for an electric field effect. At this time we have two possible template structures for field-effect transistors. The first structure starts with an aluminum wire which is anodized perpendicular to its axis to form an isolation layer onto which a gate

electrode is sputtered and then anodized again to form a network of pores parallel to the wire as a template for the synthesis of nanostructures. The nanostructures can be grown and contacted with the gate electrode already in place. Preliminary results have been obtained with tellurium nanowires. This structure is interesting for us because it can be made totally in our lab without the need for a clean room or lithography. The second structure is formed by depositing an aluminum layer on a silicon substrate which is anodized parallel to the substrate to form a lateral template for the growth of nanostructures. A gate electrode is then deposited onto the lateral template. The lateral anodization has been demonstrated with pore diameters as small as 5 nm. The advantage of this approach is that it could be implemented into existing processor fabrication. This presentation will show the first results for these approaches to field-effect transistors based on anodized aluminum templates.

GG6.27

Wafer-level Ordered Arrays of Aligned Carbon Nanotubes with Controlled Size and Spacing on Silicon.

Ramkumar Krishnan¹, Hung Quang Nguyen², Wee Kiong Choi², Foo Yong Lim³ and Carl V. Thompson¹; ¹Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Advanced Materials for Micro and Nano-systems, National University of Singapore, Singapore-MIT Alliance, Singapore; ³Institute of Materials Research and Engineering, Singapore, Singapore.

Ordered arrays of well-aligned multi-walled carbon nanotubes (CNTs) have been fabricated using perfectly-ordered porous alumina templates on silicon. Single-domain porous alumina with regular pore symmetry over an entire wafer was achieved by anodizing thin films of aluminum evaporated on nanoscale-corrugated silicon surfaces. The silicon surface was patterned using interference lithography, and periodic arrays (with hexagonal and square symmetry) of inverted pyramid structures were formed through anisotropic wet etching. Anodization of aluminum films deposited on these corrugated surfaces led to periodic pore structures with the pore spacing and symmetry determined by the pattern etched into the silicon. Nickel was evaporated into ordered alumina templates and ion-milling was used to remove the excess nickel from the surface of the porous alumina. The resulting Ni nanodots at the base of the pores catalyzed CNT growth inside the ordered porous alumina templates during plasma enhanced chemical vapor deposition with acetylene and ammonia at 700-750°C. The resulting multi-walled crystalline nanotubes were characterized using SEM, TEM and Raman spectroscopy. These results demonstrate a wafer-scale approach to control the size and position of carbon nanotubes and other nanoscale elements (including both metallic and semiconductor nanowires) in a rigid insulating scaffold. We will also discuss other wafer-level approaches to obtain aligned & ordered carbon nanotubes with sub-lithographic spacing.

GG6.28

Lithographically Fabricated Free-Standing Carbon Nanotube Specimens Embedded in Polymer. Amit Desai¹ and Aman Haque; Mechanical and Nuclear Engineering, Pennsylvania State University, State College, Pennsylvania.

We present a novel lithographic technique for fabricating free-standing carbon nanotube specimens. Our technique can also be used to fabricate free-standing specimens of other nanostructures (nanotubes and nanowires) in polymer or metal. Free-standing specimens are preferred for experiments to determine mechanical, thermal, electrical and electromechanical properties of nanotubes and nanowires and also their interaction with other material and environments like interfacial mechanics of composites. The proposed fabrication technique is based on the 'photolithography' process, which is widely used in nano-fabrication processes to create nanometer size patterns. The technique consists of dispersing nanotubes and photoresist (a photosensitive polymer) mixture on a substrate and using photolithography to define the placement and density of free-standing nanotube specimens, embedded in photoresist. The flexibility offered by the lithography method enables us to co-fabricate the nanotube specimens with sensors and actuators for performing experiments. The lithography process allows us to integrate the free-standing specimens with MEMS based sensors and actuators, which on account of the scaling (micro level) have very high resolution. The fabrication of nanotubes in polymer provides for firm gripping of the specimen, thus enhancing the quality of experimental data. The fabrication technique proposed is robust, repeatable and flexible. We have prepared free standing specimens of carbon nanotube in photoresist and are developing such specimens of carbon nanotubes for mechanical, interfacial and electromechanical testing. In order to exploit the unique length scale dependant properties of carbon nanotubes, it is essential to perform experiments to characterize carbon nanotubes to validate the related theoretical and computational research. For obtaining a reasonable estimate of the carbon nanotube properties, it is also important to conduct the experiments on a single free-standing

carbon nanotube specimen. Various challenges exist for direct experimental determination of carbon nanotube properties and their interaction with other material and environment, like integration with high resolution sensors and actuators and firm gripping of the specimen. Additionally carbon nanotubes embedded in polymer specimen are required to perform various kinds of interfacial testing; the information obtained from such experiments can be exploited for fabrication of carbon nanotube polymer composites. Carbon nanotube polymer composites are claimed to possess exceptionally good mechanical, thermal and electrical properties. However in order to exploit these properties, it is necessary to perform experiments on interfacial testing to support the claims made by theory. The information obtained from such experiments will not only aid in understanding of interfacial characteristic but will also be useful in manipulation of the interfaces for improved nanocomposites.

GG6.29

Thermally Controlled Growth of Nanowires. Tom Harris¹, Debasish Banerjee², Zhifeng Ren² and Gang Chen¹; ¹Mechanical, MIT, Cambridge, Massachusetts; ²Physics, Boston College, Chestnut Hill, Massachusetts.

Nanowires and nanotubes possess numerous attractive physical properties for potential use in electronics, photonics, sensing, and energy conversion. The synthesis of nanowires has become relatively simple using a variety of fabrication methods now available, such as vapor-liquid-solid (VLS) growth and pressure-injection-template techniques. However, despite the relative simplicity of nanowire synthesis (compared to epitaxial-film growth), nanowire devices are far from mass production. One of the key issues impeding the large-scale development of nanowire devices is that nanowires, as synthesized, are usually oriented in a random manner. Current methods for producing devices out of random nanowire arrangements typically result in one or a few proof-of-principle devices by, for example, randomly dispersing nanowires on a wafer with existing electrodes in hopes of making a few good electrical contacts. Recent attempts to place aligned wires in desired locations rely on microfluidic shear-stress flows coupled with surfactants for wire selectivity. Nevertheless, because of the low success rate in placing nanowires in desired locations and an equally low yield of viable devices, these post-nanowire growth processing methods are not practical as fabrication techniques for mass-producing devices. A different alignment approach is to orient nanowires during their growth process via external electric fields. This method employs a field similar to that used in plasma-enhanced chemical vapor deposition (PECVD) and was the first technique to demonstrate growth of carbon nanotubes and self-assembled nanowires perpendicular to the substrate. Although this wire-growth method can be advantageous, nanowires grown vertically from the substrate typically are not compatible with conventional microelectronics, which are based on in-plane devices. A few researchers have developed experiments, particularly in carbon nanotube growth, where an electric field is applied in a direction horizontal to the surface to grow nanotubes parallel to that surface. These approaches, however, have not yet succeeded in making wafer-scale devices. Our method for controlling the location and directionality of nanowire growth is based on thermally activating a single nanowire catalyst particle in the VLS process to initiate selective wire growth and placement, while employing an electric field to guide the wire in a desired direction. This technique is demonstrated using resistive heating with platinum microheaters. With this simplified approach we observe selective nanowire growth due to the locally heated region of the heater and also observe the effects of an applied electric field on wire growth directionality.

GG6.30

Highly Oriented Plate-Like Nanorods Arrays of ZnO.

Ying Dai, Yan Jin Li, Xin Mei Pei and Long Qiang Zhou; School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, China.

Highly oriented plate-like nanorods arrays of ZnO are synthesized by solution-based approach at low temperature. ZnO nanorod arrays grow oriented vertically on the silicon substrate and the nanorod consists of the pile of platelike ZnO single-crystal along the c-axis direction. The construction of platelike arrays is achieved by varying the growth conditions. The growth mechanism is analyzed by XRD, SED, TEM and HRTEM based on the nuclear and growth process of ZnO. Photocatalytic properties of the nanostructures arrays are investigated. The novel ZnO nanorod arrays are expected to have great potential for sensing, catalysis and optical emission.

GG6.31

Carbon Assisted SiOx Nanowire Growth. Yiping Zhao¹, S.-H. Li¹, X.-F. Zhu¹, Samuk Pimanpang² and G.-C. Wang²; ¹Physics and Astronomy, University of Georgia, Athens, Georgia; ²Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New

York.

During attempts to fabricate ZnO nanowires, we accidentally observed the growth of SiOx nanowires on Au coated Si substrate. Detailed characterizations on the resulting nanowires were carried out by field-emission scanning electron microscopy, transmission electron microscopy, selective area electron diffraction, X-ray diffraction, electron microprobe, energy-dispersed X-ray spectroscopy, and X-ray photoelectron spectroscopy. The resulting nanowires have a Si-to-O ratio of 1:1.63, and a diameter ranging from 50 nm - 300 nm. It was found that the presence of graphite powder in the growth furnace was critical. A systematic investigation of how the growth conditions, such as the growth temperature, the oxygen to Ar carrier gas ratio, and the growth time, affect the formation of SiOx nanowires, was performed. A high growth temperature (1000°C), and an appropriate low oxygen gas flow (250 SCCM Ar and 5 SCCM O2) helped promoting the growth of long nanowires. The diameters of nanowires increased with the growth time. It was demonstrated that the formation of the SiOx nanowires was due to a solid-liquid-solid mechanism, and a local catalytic oxidation of CO by Au nanoclusters played a role in accelerating nanowire formation.

GG6.32

Peptides with Selective Affinity for Carbon Nanotubes.

Caroline Lau¹, Yet-Ming Chiang¹ and Steve Lustig²; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Dupont Central Research and Development, Experimental Station, Wilmington, Delaware.

The use of biological molecules to facilitate the dispersal, separation and assembly of nanoscopic entities such as carbon nanotubes has received great attention and has been the focus of much current research activity. In this work we sought to identify peptide sequences with selective affinity for HiPco-produced SWNTs (single-walled carbon nanotubes) in order to gain some insight to the binding mechanisms and interactions. This was done using a phage display technique, in which a library of bacteriophages displaying greater than 10⁹ different 12-amino acid long peptide sequences were exposed to carbon nanotubes. Non-specifically bound phages were successively washed off with increasingly stronger detergents until only tightly binding phages remained. It was observed that after six rounds of phage display tests, the percentage of sites of aromatic ring-containing amino acids increased while the percentage of sites of aliphatic amino acids decreased. Results were compared to previous phage display results on MWNTs (multi-walled carbon nanotubes). These results suggest that peptides are able to distinguish between different allotropes of carbon and that their highly specific binding mechanisms can be exploited in the future for use in precision placement of nanoscale components in devices such as electronic circuits and sensors.

GG6.33

One Directional Alignment of the Metal /Oxide Hybrid Nanotube with Self-assembled Monolayers (SAMs).

Daekyun Jeong, Jaegab Lee, Hyunjung Shin and Jiyoung Kim; Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

Various fabrication methods on oxide and metal nanotubes have been investigated due to their excellent physical and chemical properties. In order to use appropriate the nanotubes, it is important to develop technology to align the nanotubes and integrate into a system. In this paper, we demonstrate a novel methodology on aligning metal/oxide hybrid nanotube in one direction can make the metal and oxide nanotube array using self-assembled monolayer(SAM) on Si wafer. We have fabricated metal/oxide hybrid nanotube using conformal and selective deposition techniques atomic layer deposition (ALD) and SAM on nanotemplates. This technique allows to fabricate nanotubes precisely on the control of wall thickness with a few tens nanometers of radius and a few micrometers of length on soluble nano-templates. We used organic base materials (polycarbonate) nanotemplate supplying uniform nano-scale pores. Then we performed surface treatment using SAM on the nanotemplate in order to achieve selective deposition. And we deposited conformal and uniform thin metal oxide tube wall using ALD. Polycarbonate nanotemplate was perfectly removed by vacuum filtering after dissolving in the solvent such as Chloroform, then metal/oxide nanotubes were wetted with hydrophilic SAMs (Hexadecanethiol:HDT). The metal/oxide nanotubes were coated with HDT. We patterned Si/SiO₂ substrates using soft contact printing with OTS (Octadecyl-tetrachlorosilane) inks which transfer Si /SiO₂ substrate properties from hydrophilic to hydrophobic property. Hydrophilic nanotubes were aligned in one direction following Si wafer line, otherwise there is no nanotubes on OTS line pattern. The various properties of the resultant metal oxide nanotube were examined with a number of techniques of HR-TEM, FE-SEM, EDX, and AFM. We also observed nanotube direction with FE-SEM and AFM.

GG6.34

Synthesis and Characterization of GaN/InGaN/GaN Radial Core/Shell Nanowire Heterostructures. Silvija Gradecak¹, Yat Li¹, Fang Qian¹ and Charles M. Lieber^{1,2}; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Compositionally modulated nanowires are attractive building blocks for nanophotonics and nanoelectronics. For example, control of the structure and composition during nanowire synthesis can define their photonic properties, such as emission wavelength or color. Here we report growth and structural investigations of radially-modulated GaN/InGaN/GaN core-shell-shell (CSS) nanowires, whose composition variation can provide light emission in the 0.8-3.5 eV energy range. GaN nanowires were first grown by a nanocluster-mediated growth, and then sequentially over coated by InGaN and GaN nanoscale shells. All of the growth steps were carried out continuously using metal-organic chemical vapor deposition. Bright-field transmission electron microscopy (TEM) images combined with energy dispersive X-ray spectroscopy (EDX) demonstrate (i) diameter control of the starting GaN nanowires by the size of the catalytic nanoparticles and (ii) epitaxial growth of the shells. These TEM studies further reveal defect-free CSS nanowire structures, which should provide a unique advantage compared to dislocation-rich, GaN-based planar structures. Electron diffraction and high-resolution TEM images show that the CSS nanowires have a wurtzite structure, {11-20} growth direction, and triangular cross-section defined by {0001} and two {1-101} crystallographic planes. These data were used to construct a CSS structural model that successfully fits EDX compositional line profiles, and allows calculation of the core and shell thickness. Taken together, these data demonstrate that GaN/InGaN/GaN CSS nanowires were grown having single crystal and dislocation-free structure, smooth surface and radially modulated composition. The high yield and compositional control of GaN/InGaN/GaN CSS nanowires achieved in our work provide an essential step towards future nanoscale applications, such as nanoscale light emitting diodes and lasers.

GG6.35

Generic Synthesis of Transition Metal Oxide Core-Shell Nanowires. Song Han, Chao Li, Zuqin Liu, Bo Lei, Daihua Zhang and Chongwu Zhou; EEEP, University of Southern California, LA, California.

A generic non-equilibrium synthesis technique is presented to produce a wide variety of core-shell transition metal oxide nanowires. The key of the technique is the preparation of vertically aligned MgO nanowires to work as the core material. The growth was conducted at 900 degree C on MgO (100) substrates coated with monodispersed gold clusters. Mg₃N₂ powder worked as the feedstock, and SEM images of as grown MgO nanowires revealed that all the nanowires were normal to the substrate. These vertical nanowires were then used as templates for pulsed laser deposition of the desired transition metal oxides, including YBa₂Cu₃O_{6.66} (YBCO), La_{0.67}Ca_{0.33}MnO₃ (LCMO), PbZr_{0.58}Ti_{0.42}O₃ (PZT) and Fe₃O₄. These four material systems represent a broad collection of physical properties, as YBCO is a well-known high T_c superconductor, LCMO exhibits intriguing colossal magnetoresistance, PZT is an important ferroelectric material and Fe₃O₄ is a spin half-metal that is under intensive studies. Built upon the knowledge accumulated in the past decades on metal oxide film studies, this technique yielded single crystalline core-shell MgO/transition metal oxide nanowires with precisely controlled layer thickness. Transport studies on a 10 nm thick LCMO nanowire has revealed pronounced magnetoresistance with a transition temperature 170 K and magnetoresistance ratio approaching 70%. Our technique will enable the phase transition studies in nanoscale transition metal oxide nanowires and may pave the way for various novel applications.

GG6.36

Abstract Withdrawn

GG6.37

One-step Chemical Synthesis of High-aspect-ratio Gold Nanorods. Lihua Pei, Fumin Wang, Jinting Jiu and Motonari Adachi; Institute of Advanced Energy, Kyoto University, Uji, Kyoto, Japan.

Abstract: This paper describes a simple and novel procedure for the fabrication of gold nanorods with aspect ratios over 100 under mild conditions. The procedure involves just one-step chemical reduction reaction in which NaAuCl₄ is reduced with tri-sodium citrate in the presence of cetyltrimethylammoniumbromide (CTAB) acting as shape-inducing surfactant. Controlled amount of NaOH must be added into the reaction solution, without which the reduction reaction could not be initiated. After the addition of NaOH, the yellow

solution which is characteristic of complex of CTAB and AuCl₄ became colorless instantly, indicating the reduction of Au³⁺ to Au⁺. Subsequently, this solution gradually turned pink, purple and purple-red in a different time period with varying amount of NaOH. At reaction temperature of 80 centigrade, gold nanorods with aspect ratio over 100 could be obtained when the pH value was controlled at about 9-10. Lower or Higher than this value could lead to the products of gold nanoparticles with spherical or triangle shapes. We controlled the conditions for the formation of gold nanorods through a process of nucleation and subsequent growth into nanorods with capping of CTAB on specific crystalline facets. Key factors, such as temperature, pH value, CTAB concentration and reaction time, are expected to greatly affect the aspect ratio and yield of the gold nanorods. Thus careful control of the reaction condition is important for obtaining target product. The details about the formation mechanism will be presented at the presentation. This process is very simple, without any aid of seeds or additives during the formation process, and expected to be suitable for the large-scale synthesis.

GG6.38

Registering the two-dimensional positions of block copolymer domains on substrates using templated self-assembly.

Joy Y. Cheng¹, Henry I. Smith² and Caroline A. Ross¹; ¹Materials Science & Engineering, MIT, Cambridge, Massachusetts; ²Electrical Engineering and Computer Science, MIT, Cambridge, Massachusetts.

The creation of two-dimensional ordered nanostructures with precise positional registration on a substrate is important for devices such as patterned magnetic media and plasmonic waveguides. Block copolymers are well-known examples of self-assembling systems, in which chemically distinct blocks phase-separate into nanoscale periodic domains. As thin films, these nanostructures can be ideal templates for creating large-area two-dimensional nanostructures. In this study, we investigate the effectiveness of pattern registration of 2D self-assembled spherical block copolymer polystyrene (PS) -b- polyferrocenyldimethylsilane (PFS) arrays formed on substrates with shallow topographical trenches. These shallow trenches act to confine the 29 nm-period polymer sphere array within areas with widths from 50 nm to 500 nm and lengths of tens of microns. Within each proper trench, well-ordered arrays of spheres form with rows of spheres parallel to the edges of the trenches. (Cheng et al, *Advanced Materials* 19, 1599 (2003)). In this work we investigate how well the lateral positions of the spheres in the array can be controlled or 'registered' by the introduction of small jogs or roughness at the edges of the trenches. The effectiveness of pattern registration was characterized by measuring the translational correlation function of the polymer arrays parallel to the edges of the trenches from digitized scanning electron micrographs. Our study shows that the translational correlation length increases as the trench width decreases from 500 nm to 300 nm, and as the amplitude of the line-edge roughness of the trenches increases. This shows that the stronger confinement of the array that is present in narrower trenches creates better ordering along the unconfined length direction of the groove. In the direction of confinement, the translational correlation length decreases as the distance from the registration marks on the edge of the trenches. Models for this behavior will be presented and can be used to design trenches for the registration of nanostructure arrays across large regions of the substrate. A nanostructure array with longer correlation length requires fewer registration marks to sustain global positional registration over a large area. A design window will be given to demonstrate the advantages and the limitations of registering self-assembled nanostructures using topographical templates.

GG6.39

Self-Reorganization of Semiconductor Nanoparticles. Zhiyong Tang, Ying Wang and Nicholas A. Kotov; Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

A novel strategy to synthesize one-dimensional nanowires with hierarchy structures is explored. Meso-stable CdTe nanoparticles are used as reaction sources for further self-reorganization process. By judicious control over the experimental conditions, variable advanced shapes of nanowires, such as thread, core in shell, wire in tube, particle embedded in wire, have been successfully produced. Possible formation mechanism will be discussed, and unique advantage of nanoparticles as source will be disclosed.

GG6.40

Abstract Withdrawn

GG6.41

Template-directed growth of nanoparticle-mediated colloidal crystals on large-area patterned substrates generated by multibeam holography. Ryan J. Kershner¹, Summer K. Rhodes², Vinayak Ramanan², Paul V. Braun^{1,2}, Jennifer A. Lewis^{2,1} and Pierre Wiltzius^{1,2}; ¹Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Department of Materials

Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Large-domain colloidal crystals were created by gravitational settling of colloidal microspheres onto patterned substrates. The large-area patterned substrates were produced using multibeam-beam interference lithography, facilitating templated epitaxial growth of single domain crystals with controlled crystallographic orientation. A 2-beam UV laser setup was employed to produce 1-D features with a periodicity on the order of 500 nm (colloid diameter). This was extended to a square array of 2-D features through multiple exposures or multiple beams. Atomic force microscopy (AFM) was used to characterize the resulting surface structures. The exposure parameters were varied to control the depth and width of the features in an attempt to optimize the pattern for defect free colloidal epitaxy. Colloidal crystals were produced from a binary suspension of colloidal microspheres stabilized through the addition of highly charged nanoparticles (Tohver et al., PNAS (2001)) followed by subsequent nanoparticle gelation (Lee et al., Langmuir (2004) to yield robust structures that can withstand capillary forces during drying.

GG6.42

Synthesis and Self-Assembly of Hydrogel Nanoparticles with Interpenetrating Polymer Networks. Xiaohu Xia and Zhibing Hu; Physics, University of North Texas, Denton, Texas.

Monodisperse nanoparticles composed of poly-acrylic acid (PAAc) and poly(N-isopropylacrylamide) (PNIPAM) interpenetrating polymer networks (IPN) were synthesized by two-step method with first preparing PNIPAM nanoparticles and then polymerizing acrylic acid that interpenetrates into the PNIPAM network. The growth kinetics of the IPN particle formation was obtained by measuring the turbidity and particles hydrodynamic radius (Rh) as a function of reaction time. Individual IPN and PNIPAM nanoparticles were characterized and compared using dynamic and static light scattering techniques. The concentrated aqueous solutions of the PNIPAM-PAAc IPN nanoparticles can change from a fluid at room temperature to a physically bonded nanoparticle network above a gelation temperature about 33 °C. The PNIPAM provides physical bonds between particles via a temperature-dependent interparticle potential, while PAAc in the neutral pH provides ionic charges that are temperature-independent and prevent the collapse of the particles into an aggregate. This system exhibits a very rich phase behavior including a colloidal crystalline phase in which the system displays iridescent colors.

GG6.43

The Assembly of Gold Nanoparticles at Liquid-Air Interface and Application in Surface Enhanced Raman Spectroscopy. Tao Deng, Amy Linsebigler, Darryl Williams, Eric Olson and Peter Codella; Nano Advanced Technology, Global Research Center, General Electric, Niskayuna, New York.

Dispersed in an aqueous solution, gold nanoparticles can self assemble into films at the liquid-air interface when another solvent(s) is introduced into the solution. Many approaches have been reported for forming self assembled nanoparticle films in solution, but most of them involve the modification of nanoparticle surfaces before the film forming process. For example, coating the nanoparticle surfaces with alkanethiols will reduce the solubility of the nanoparticles in water and drive them to the liquid-air interface to form two-dimensional films. In this presentation, we demonstrate a new approach for the self-organization of gold nanoparticles at the liquid-air interface. This approach does not require the extra step for the modification of the gold nanoparticle surfaces. Gold nanoparticles, with sizes from 5 nm to 100 nm, are directly synthesized in an aqueous solution. A second solvent is then introduced into the solution in a carefully controlled fashion. The originally well-dispersed gold nanoparticles will self-assemble into two-dimensional films at the liquid-air interface. When transferred onto solid substrates, these films are ideally suited as substrates for surface enhanced Raman spectroscopy (SERS). Compared to SERS active nanoparticles suspended in solution, these solid thin film substrates can sustain the change of pH, solvents, etc., in the detection process using SERS. When they are exposed to gaseous target molecules, these thin films can also give intense Raman signal.

SESSION GG7: Micro- and Macro-assembly Strategies
Chairs: James Hutchison and Gerard Wong
Wednesday Morning, December 1, 2004
Room 311 (Hynes)

8:30 AM *GG7.1

Directed Assembly of Materials from Nanoscale Building Blocks. Richard W. Siegel, Rensselaer Nanotechnology Center and

Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York.

Great strides are now being made in our ability to assemble nanoscale building blocks to create advanced materials with novel properties. A perspective of this important area in materials research will be presented based upon specific examples from our work in the Center for Directed Assembly of Nanostructures supported by the Nanoscale Science and Engineering Initiative of the U.S. National Science Foundation. The presentation will include examples of directed assembly of nanoparticles, nanotubes, and hybrid structures containing these and biomolecules to make new materials with enhanced mechanical, electrical, optical, and bioactive properties, and multifunctional combinations thereof. The opportunities and challenges facing the nanostructured materials research community in moving forward in this area will be considered.

9:00 AM GG7.2

Nanoparticles' Assemblies from Chains to Rings: A New Approach Towards Covalently Bound Nano-Objects.

Markus Brunnbauer, Benjamin H. Wunsch, Brian T. Neltner, Alicia M. Jackson and Francesco Stellacci; MIT, Cambridge, Massachusetts.

Size dependent optical, electronic and physical properties of nanoparticles, nanorods and nanowires not only depend on their dimensions but the also critically depend on their assembly. It is known, for example that surface plasmon absorption of a metal nanoparticle is different in the case of an isolated particle, a particle within a chain and a particle in a two dimensional lattice. Among all the nanomaterials monolayer protected metal-nanoparticles (MPCs) are particularly interesting because, by changing the molecules that compose their ligand shell, it is, not only possible to change and control the overall material properties, but also to induce given assembly properties. Here we show how recently discovered mixed monolayer protected nanoparticles, that show ordered domains in the ligand shell,[1] can be chemically modified in specific equatorial spots of their sphere. By placing in such spots molecules that have chemically reactive end groups it is possible to induce the assembly of nanoparticles in a controlled fashion. For example, by placing two carboxylic acid terminated molecules in diametrically opposed position on a nanoparticle, and by reacting such particles with di-amine terminated molecules it is possible to generate long chains of particles. Control over the numbers and relative position of the molecules placed on the nanoparticles enables us to produce chains, rings and other shapes of particles. Alternating amino functionalized and carboxylic acid functionalized nanoparticles allows the synthesis of chains of alternating types of particles, e.g. silver/gold chains. Chains of nanoparticles with cores bigger than 15 nm with a core to core distance of 3nm are potential candidates for use in surface enhanced Raman spectroscopy (SERS). Indeed preliminary results in this direction will be discussed. 1 A. Jackson, J. Myerson, and F. Stellacci, Nature Materials 2004, 330

9:15 AM *GG7.3

On-chip Electric Field Driven Assembly of Microparticles, Nanoparticles and Live Cells. Orlin D. Velev, Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

Dielectrophoresis, particle polarization and mobility in alternating electric fields, allows manipulation and controlled assembly of colloid particles. We use electric fields to make particle structures directly above planar on-chip electrodes and to interface them with electrical circuits. We will report how microparticles, nanoparticles and live cells can be assembled in 1D chains and 2D arrays by the use of AC fields. The simplest type of particles that we have studied is dielectric latex or silica microspheres. The combination of dielectrophoresis and dipolar chaining leads to the formation of single-domain centimeter sized photonic crystals with specific orientation. Such electrically switchable crystals act as rudimentary photonic devices, and allow studying the interactions and phase transitions in particle ensembles. Dielectrophoresis can also be used to assemble metallic nanoparticles into electrically conductive microwires. The dynamics of the process can be modeled, and the microwire growth direction can be steered to make self-assembled "wet" circuits. The natural extension of these principles is the assembly of live cells. Chains and membranes from yeast cells were prepared between electrode pairs and the optimal conditions in terms of field and frequency were identified. We will also demonstrate how by balancing the induced dipole interactions the process can be extended to co-assembly of cells and synthetic particles. The biocomposite arrays obtained by dielectrophoretic assembly techniques can be used as components of sensors and microreactors.

9:45 AM GG7.4

Nanopatterning of Polymer Brushes by Scanning-Probe and Electron-Beam Lithography. Woo Kyung Lee¹, Marian Kaholek¹,

Sang Jung Ahn², Kenneth C. Caster¹, Bruce LaMattina³ and Stefan Zauscher¹; ¹Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; ²Computer Science, Duke University, Durham, North Carolina; ³Army Research Office, Research Triangle Park, North Carolina.

Here we present several lithographic approaches that we have adopted to fabricate nanopatterned polymer brushes. We demonstrate the use of nanoshaving, where an atomic force microscope (AFM) cantilever tip is employed as a nanomechanical tool to selectively remove a thiol resist. The freshly exposed gold surface in the resulting nano-trenches was immediately backfilled with a bromo-thiol initiator and enabled patterned surface initiated polymerization. In a complementary approach we prepared oxide nanopatterns on resist-coated silicon surfaces by applying an electric potential between the AFM cantilever tip and the silicon substrate. In this case the nanopatterns were backfilled with a silane initiator SAM. We show that the choice of silane SAM enables both, ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP). We also used lift-off (dissolution) e-beam lithography (EBL) to generate gold nanopatterns that could again be used to immobilize a thiol initiator. The resulting patterns are then amplified by surface-initiated polymerization (bottom-up) from immobilized thiol initiator. We demonstrate that by choosing an appropriate nanolithography technique and combining it with a suitable polymerization technique allows us to fabricate high-density polymer brush arrays with control over chemical functionality, feature dimension, shape, and interfeature spacing on the nanometer length scale. We believe that we are the first to show that brush height depends sensitively on the size of the characteristic dimension of the initiator nanopattern. This behavior potentially has significant consequences for the design and fabrication of nanopatterned polymer brushes. Furthermore we demonstrate that the spatially controlled immobilization of stimuli-responsive macromolecules on solid surfaces at the nanometer-length scale enables fabrication of smart externally switchable polymer nanoarrays. Such nanostructures can provide sensing functionality within integrated nanoscale bioanalytical devices in which the transport, separation, and detection of biomolecules must be performed in aqueous solutions.

10:00 AM **GG7.5**

Surface tension based self-assembly of nano and micro 3D structures. David H. Gracias, Zhiyong Gu, Michael Yang and Yiming Chen; Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

The talk will describe results in the assembly of 3D structures ranging from nanowires to micropolyhedra using surface tension. Nano and micro scale components are fabricated using a combination of conventional and unconventional methods of fabrication. These include photolithography, etch as well as electrodeposition in templates. The components are functionalized using self-assembled monolayers that alter the interfacial characteristics of the components. Components are assembled in a fluidic medium under agitation. Specifically this talk will describe strategies and methods for the assembly of 3D structures with relevance to microelectronics.

10:30 AM ***GG7.6**

Directed Assembly of 3D Mesoscale Architectures from Nanoscale Building Blocks. Jennifer A. Lewis, Materials Science, University of Illinois, Urbana, Illinois.

We have developed a novel approach to patterning 3D periodic mesostructures via direct-write assembly of nanoparticle and polyelectrolyte inks. Central to our approach is the creation of concentrated inks that can flow through fine deposition nozzles and yet "set" almost instantaneously to facilitate shape retention as they span gaps in underlying layers. Complex 3-D structures with feature sizes ranging from 0.5 to 100 microns are assembled by direct writing using a 3-axis, motion-controlled robotic stage. These 3D periodic mesostructures may find potential application as functional and structural composites, or templates for photonic materials and sensors.

11:00 AM ***GG7.7**

Smart Nanostructured Materials by Sequential Layering: From Photonics to Ultrastrong Material and Tissue Engineering. Nicholas Alexander Kotov, ¹Chemical Engineering, University of Michigan, Ann Arbor, Michigan; ²Materials Science, University of Michigan, Ann Arbor, Michigan; ³Biomedical Engineering, University of Michigan, Ann Arbor, Michigan.

Layered nanocomposites with high degree of organization can be prepared from polymers and a variety nanocolloids such as nanoparticles, nanowires, nanotubes, clay platelets, and proteins by means of a new thin film deposition technique known as layer-by-layer assembly (LBL). (Sub)monolayers of the organic and inorganic materials are deposited in regular stacks determined by the deposition

protocol. Control of distance and orientation of nanocolloids in the multilayers affords fine-tuning of the composite properties – optical, electronic, mechanical and biological. Recent examples of composite materials with unique characteristics include optically active thin films from nanoparticles, and ultrastrong materials from single wall carbon nanotubes (SWNT), carbon fibers, and clay platelets. Immobilization of the SWNTs in the composite in each adsorption cycle prevents phase separation and makes the distribution of the nanotubes highly uniform. The successful deposition of the multilayers with complex nanostructures can also be extended toward biological applications, which include implantable sensors and artificial tissues.

11:30 AM **GG7.8**

In-situ Synthesis and Directed Assembly of Gold Nanoparticles of Different Shape from Spatially Constrained Surfactant Aggregates. G. Ramanath¹, Ashvani Kumar¹, Vivek Agarwal², Arijit Bose² and Vijay John³; ¹Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Department of Chemical Engineering, University of Rhode Island, Kingston, Rhode Island; ³Department of Chemical Engineering, Tulane University, New Orleans, Louisiana.

We demonstrate a novel surfactant-aggregate templated in situ technique to synthesize and direct the assembly of hexagonal and triangular gold nanoparticles by harnessing component molecules in the aggregates as reducing agents. This method obviates the use of external reducing agents and opens up new possibilities for realizing materials filled with organized assemblies of nanostructures. Metal nanoparticles exhibit unique shape dependent optical properties such as enhanced fluorescence in gold nanorods and quadrupole plasmon resonances in silver nanoprisms, making them attractive for optical nanodevice concepts and applications. A number of protocols have been developed to modulate the nanoparticle shape. While most protocols result in predominantly rod-like nanoparticles or nanofibers of tunable aspect ratios, faceted morphologies, e.g., triangular or flat hexagonal particles have been observed less frequently. Here, we synthesize faceted gold nanoparticles without using any external reducing agents such as citric acid or sodium borohydride. Adding an aqueous gold chloride into a AOT/Lecithin/isooctane mixture results in gelation and formation of spatially constrained microemulsions of different shapes depending upon the water content. The charged surfactants in the constrained environment reduce gold ions, and serve as a capping agent, resulting in nanoparticles of triangular or hexagonal shapes. The nanoparticles and their assemblies have been characterized by cryo- and conventional transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared Spectroscopy (FTIR), UV-visible Spectroscopy and Nuclear magnetic Resonance (NMR) spectroscopy. Based upon our measurements, we propose a phenomenological model to describe the relationship between the synthesis and assembly process parameters and particle shape and assembly structure.

11:45 AM **GG7.9**

Microemulsion-Based Synthesis of Stacked Calcium Carbonate (Calcite) Superstructures. Chulanapa Viravaidya, Mei Li and Stephen Mann; Chemistry: Inorganic and Materials department, Bristol university, Bristol, United Kingdom.

The synthesis of organized extended structures based on the assembly of nanostructured building blocks is currently recognised as an important theme at the nano-micro interface. Complex macroscopic structures consisting of self-organized surfactant-inorganic nanofilaments of BaSO₄, BaCrO₄, BaCO₃, CaSO₄, or CaCO₃ can be synthesized in water-in-oil microemulsions by emergent processes involving nucleation and growth within aggregates of surfactant-coated amorphous inorganic nanoparticles. Recent studies on calcium carbonate crystallization in microemulsions have shown that different polymorphs with higher-order complex architecture can be prepared by changes in the reactant molar ratio, number ratio of water droplets per nanoparticle (*n*), and size of the microemulsion water droplets as defined by the $w = [H_2O]/[surfactant]$ value. In this communication we report the spontaneous formation of novel complex architectures of the thermodynamically stable calcium carbonate polymorph, calcite, by addition of sodium carbonate-containing NaAOT microemulsions (*w* = 40) to reverse micelles of calcium dodecylbenzenesulfonate under conditions of high alkalinity (pH = 11) and [Ca²⁺] : [CO₃²⁻] molar ratio of 1.4 : 1. SEM studies revealed that the precipitated material consisted of stacked arrays of ca. 20 nm-thick plate-like calcite crystals with pseudo-hexagonal morphology. Significantly, high magnification SEM images showed close morphological alignment of the plates, suggesting the presence of strong interparticle contacts between adjacent lamellae. Electron diffraction also indicated some degree of crystallographic coherence between the adjacent lamellae. Patterns recorded from stacks that consisted of less than four well-defined plate-like lamellae and viewed end-on showed either a single [001] zone pattern or a superimposition of [001] zone patterns that were very closely aligned with an angular

deviation of less than 10° . The data were therefore consistent with a structural model for the stacked arrays in which the calcite plates were aligned along a common crystallographic c axis and co-aligned azimuthally along their a and b axes. Finally, it is interesting to note that the stacked calcite superstructures resemble the morphology and organization of aragonite crystals secreted in the nacreous layer of mollusc shells. Although the polymorphs are different, both architectures consist of plate-like crystals with {001} faces that exhibit spiral growth patterns, and which are interspaced with organic molecules and stacked along a common c axis. In this regard, the generation of stacked calcite superstructures in microemulsions not only provides a novel route to complex synthetic materials but also supports the notion that controlled crystallization rather than oriented aggregation is a feasible mechanism for the formation of oriented lamellar composites in biomineralization.

SESSION GG8: Theoretical Aspects of Structure and Properties of Nanounits and Mesoassemblies
Chairs: Arijit Bose and Mauricio Terrones
Wednesday Afternoon, December 1, 2004
Room 311 (Hynes)

1:30 PM **GG8.1**

Molecular Simulation of Mesoscale Architectures Assembled from Patterned Nano Building Units. 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 a materials revolution in which entirely new classes of fundamental building units will be designed and fabricated with desired features, including programmable instructions for assembly. Already, many proof-of-concept demonstrations exist. For example, synthetic chemistry now provides the possibility of designing molecular and nanocolloidal building blocks of matter with anisotropic interactions due to anisometry, 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. However, in contrast to traditional materials, little is known about the properties of these new building blocks, the forces between them controlling their assembly into target structures and bulk phases, and the properties of these assemblies. We seek to develop a theoretical framework for predicting the self-assembled structures that result from nano building blocks patterned or functionalized with organic and biomolecule ligands. In this talk, we present results of molecular simulations and Monte Carlo simulations of self-assembly of model patterned building blocks, and show how building block shape and topology, pattern anisotropy, and cognitive interactions can be exploited to achieve complex mesoscale one-, two- and three-dimensional structures such as wires, sheets, junctions and shells [1-4]. We apply geometric packing rules and discuss their opportunities and limitations for predicting equilibrium structures. We investigate the interplay between assembly thermodynamics and kinetics and explore transformations between ordered structures under changes in thermodynamic and external fields. We further investigate via simulation the stability of assembled structures with respect to various fabrication limitations of the building blocks [6], for applications to nanoelectronics, nanocomputation, storage. [1] Z.L. Zhang and S.C. Glotzer, Self-assembly of patchy particles, *Nano Letters*, accepted. [2] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, Tethered nano building blocks: Toward a conceptual framework for nanoparticle self-assembly. *Nano Letters*, 2003. 3(10): p. 1341-1346. [3] T. Chen, M.H. Lamm and S.C. Glotzer, Monte Carlo simulations of biomolecule-directed assembly of nano building blocks, *J. Chem. Phys.*, in press. [4] M.A. Horsch, C.R. Iacovella, Z.L. Zhang and S.C. Glotzer, preprint. [5] S.L. Teich-McGoldrick, Z.L. Zhang and S.C. Glotzer, preprint. This work is supported by grants from the NSF (CTS-0210551), and the DOE (DE-FG02-02ER46000 and DE-FG02-03-ER46094).

1:45 PM **GG8.2**

Computational Studies of Anatase Nanocrystals. Serkan Erdin³, Amanda Barnard², You Lin³, Peter Zapol^{1,2} and J. Woods Halley³;

¹Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois; ²Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; ³School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota.

Titanium oxide nanoparticles and their assemblies have attracted a lot of interest due to their potential in photochemical applications. The theoretical modeling of nanoparticle units is a computational

challenge because the systems of interest are not periodic and not small, typically having 10^4 atoms or more. A self-consistent tight-binding (SCTB) method that could be used to treat systems of this size has been parameterized for anatase and applied to a faceted anatase nanoparticle of the size of about 1 nm (105 atoms). The results have been compared for structure relaxation of the same nanoparticle performed by first-principles density functional theory. Optimized geometries at both levels of theory show good agreement. We have also compared results on nanoparticle cohesive energies and electronic charge distributions. For the latter, we have performed calculations of both electron charge density and electron localization functions in the density functional study. Following validation of the results, larger nanoparticles (2 - 3 nm) were studied using tight binding methods. These units are suitable for studies of the assembly processes via molecular dynamics simulations, which will help to understand properties of anatase-based nanoarchitectures.

2:00 PM ***GG8.3**

Magnetic Properties of Carbon Nanostructures: The Role of Negative and Positive Curvature. Humberto Terrones, Julio A. Rodriguez-Manzo, Florentino Lopez-Urias and Mauricio Terrones; Advanced Materials, IPICYT, San Luis Potosi, San Luis Potosi, Mexico.

A π -orbital nearest-neighbor tight-binding Hamiltonian in conjunction with the London approximation is used to study uniform external magnetic field effects on different graphitic nanostructures with negative and positive Gaussian curvature. Ring currents and the induced magnetic moment are calculated on coalesced C60 structures (peapod-like corrugated nanotubes) and Haekelite-tubules (structures containing heptagons, hexagons and pentagons of carbon). It is found that coalesced C60 fullerenes connected along the five-fold symmetry axes and Haekelites tubes are metallic and exhibit large magnetic moments. These results have important implications in the magnetic properties of corrugated carbon nanotubes (coalesced peapods). The magnetism observed experimentally in rhombohedral C60 is also discussed in the context of ring currents generated by the sp^2 polymerization of C60. Finally, the possibility of witnessing magnetism in interconnected graphene layers is also studied.

2:30 PM ***GG8.4**

Plastic to Superconducting Properties of Silicon and Carbon Nanostructured Clathrates. Xavier Blase, Laboratoire de Physique de la Matière Condensée et des Nanostructures, CNRS and University Lyon I, Villeurbanne, France.

Column-IV semiconducting clathrates are nanostructured crystals composed of face sharing clusters. Therefore, in such systems, the building unit is not the atom but small semiconductor cages. While all atoms are in the four-fold sp^3 hybridization, as in the diamond phase, the cage structure induces the presence of a large number of pentagons in the network and the possibility of endohedral doping (or intercalation) by placing atoms at the center of the cages. Such a unique topology induces original properties that we study by means of ab initio techniques. It is shown in particular that: a) endohedral doping of silicon clathrates can open a direct band gap in the visible range (from 1.9 to 2.4 eV, GW value), opening the way to an all-integrated silicon-based opto-electronic technology [1]. b) the observed 8 K superconductivity in baryum doped Si-clathrates is found to be an intrinsic properties of the sp^3 silicon network. The electron-phonon (e-ph) coupling is strong ($\lambda \sim 1$) and, in the case of the carbon clathrates, the e-ph potential is shown to be much larger than in the fullerenes [2]. The strength of the e-ph coupling in carbon-clathrates, doped-diamond and small radius nanotubes are compared. c) the ideal strength of the carbon clathrates is shown to be superior to that of diamond in its "weak" $\langle 111 \rangle$ tensile or shear directions due to the frustration of the diamond-to-graphite instability by the clathrate cage-like structure [3]. This provide a first explanation for the repeated observation that cage-like carbon materials, such as polymerized fullerenes, can "scratch" diamond and provides new criteria for realizing ultra-hard materials. [1] D.Connetable, V.Timoshevskii, E.Artacho, X. Blase, *Phys. Rev. Lett.* 87, 206405 (2001) [2] D. Connetable et al., *Phys. Rev. Lett.* 91, 247001 (2003) [3] X. Blase, Philippe Gillet, A. San Miguel, and P.Melinon, *Phys. Rev. Lett.* 92, 215505 (2004)

SESSION GG9: Structure and Intrinsic Properties of Assemblies I

Chairs: G. Ramanath and Francesco Stellacci
Wednesday Afternoon, December 1, 2004
Room 311 (Hynes)

3:30 PM ***GG9.1**

Investigations of Thermodynamic Properties of Phase Transitions in Nanometer Scale Systems. Leslie H. Allen,

This talk focuses on characterization of the thermodynamics properties of three thin film systems including metals nanostructures, ultra-thin polymers layers, and self-assembled monolayers (SAMs) by measuring C_p via nanocalorimetry MEMS devices [1,2]. We first discuss the melting point depression of indium nanostructures[4], which consist of self-assembled indium clusters whose melting temperatures T_m are strongly influenced by size. T_m decreases linear with curvature ($1/r$) as does the values for the heat of fusion. We also found multiple peaks in $C_p(T)$ at regular temperature intervals, which can be related to quantized increments of size - one monolayer of atoms[3], a phenomenon analogous to the "magic numbers" distributions observed in cluster beams studies. The second material system is the size-dependence of glass transition in thin spin-cast polymer films on a platinum surface[5]. We observe (unexpectedly) pronounced glass transition at thickness even as small as 1-3 nm. The glass transition is assigned via the limiting fictive temperature T_f and is found to be almost size-independent ranging from 100nm to 3nm. The evolution of transition is discussed in terms of broadening of transition dynamics. The strength/contrast parameter of the transition remains strong throughout the thickness range and decreases with a characteristic length-scale value of about a 1nm. The third materials system discussed is SAMs[6]. We observe the melting/order-disorder transitions of 2D and 3D C16 SAMs grown on polycrystalline Au surfaces via C_p measurement. The amount of SAMs is typically in the 10 picomole range. The transition for the 2D SAMs occurs over a broad temperature range (100°C) with a transition temperature T_p of about 70°C. 2D SAMs, in their as-deposited state before desorption, have an even larger T_p 125 °C. The heat of transition is about 20 kJ/mol. The nanocalorimetry measurements of 3D SAMs on Au nanoparticles are comparable to earlier studies using conventional calorimetry. [1]M. Y. Efremov et al, "Ultra-Sensitive Thin-Film Differential Scanning Calorimeter", Rev. Sci. Inst., 75, 179 (2004). [2]E. A. Olson, et al, "The Design and Operation of a MEMS Differential Scanning Nanocalorimeter for High-speed C_p Measurements of Ultra-thin Films", IEEE J. Microelectromech. Sys. V13, 355 (2003). [3]M. Y. Efremov, et al., "Discrete Periodic Melting Points in Nanostructures", Phys. Rev. Lett., 85, 3560 (2000). [4]M. Zhang, et al., "Melting Point Depression of Nanostructures using Nanocalorimetry", Phys. Rev. B, 62, 10548 (2000). [5]M. Y. Efremov et al, " T_g of ultra-thin polymer films", Phys. Rev. Lett., 91, 85703 (2003). [6]Z. S. Zhang et al., " C_p Measurements of 2D SAMs on Polycrystalline Gold", Appl. Phys. Lett., 84, 5198 (2004)

4:00 PM *GG9.2
Microstructure Evolution and Materials Synthesis in a Self-Assembled Mixed-surfactant Mesophase. Arijit Bose,

¹Chemical Engineering, University of Rhode Island, Kingston, Rhode Island; ²Chemical Engineering, Tulane University, New Orleans, Louisiana; ³Chemistry, Tulane University, New Orleans, Louisiana.

Soft nanoscale materials, such as micelles, vesicles, microemulsions, liquid crystals and other complex fluids are becoming increasingly important from both a scientific as well as an applications perspective. Visualization of these materials is a challenge because of their size (2 to 100nm), their low electron density and because their aggregation state and morphology is critically dependent on solvent concentration. Several examples of artifact free visualization of soft nanoscale materials will be provided. These include reciprocal space imaging using Small Angle Neutron Scattering (SANS), as well as direct imaging using cryogenic Transmission Electron Microscopy (cryo-TEM) and Freeze Fracture Direct Imaging (FFDI). Advantages and limitations of each of these techniques, as well as how they complement each other, will be discussed. A novel transformation from a microemulsion to a gel phase has been observed by increasing the water content of a system consisting of AOT and lecithin in isoctane. Small angle neutron scattering (SANS) patterns are consistent with models that describe the microstructure as columnar hexagonal at lower water contents and temperatures, and lamellar at higher water contents and temperatures. These structures can be aligned using shear, are thermally reversible, and have been used as robust templates for a variety of reactions in the aqueous and organic nanochannels. The morphology of the nanostructured phases mimics the underlying structure of the surfactant aggregates. This feature opens up several opportunities for template-directed materials synthesis, and several examples will be shown.

4:30 PM GG9.3
Formation of Ceramic Nanosheet Using Water Layers in Lamellar Phase as A Reactive Confined Field In Situ Measurement of SAXS by Synchrotron Radiation-
Motonari Adachi, Institute of Advanced Energy, Kyoto University, Uji, Japan.

Mixed solution of surfactant (Alkylamine (AA)) and metal-alkoxide (MA) was contacted with water. Lamellar structure composed of

surfactant and ceramic oxide was formed at the liquid-liquid interface, and ceramic nanosheet such as TiO₂, SiO₂, and GeO₂ was synthesized. These nanosheets were characterized by transmission electron microscope images, selected area electron diffraction (SAED), and X-ray diffraction (XRD). XRD and SAED results showed that GeO₂ nanosheet had tetragonal crystal, which conformed to the square shape of GeO₂ nanosheets. In situ small angle X-ray scattering measurement was carried out every second for several minutes using strong X-rays by synchrotron radiation in the SPring 8, and the formation processes of ceramic nanosheet was examined. When the mole ratio of Ge(OEt)₄ to AA was adjusted to 0.2, the peaks corresponding to lamellar phase appeared at 2.5 sec after contact and increased with time. The periodical distances of the lamellar phases were almost constant, being from 3.6 nm to 3.8 nm, which corresponded to the thickness of bilayer composed of surfactant molecules. The peak shape of the lamellar phase in SAXS measurement changed from 100 % Gaussian distribution at 2.5 sec to 100% Lorentz distribution after 25 sec to 180 sec from contact. These findings indicate that highly crystallized ceramic nanosheets can be synthesized when the suitable surfactant molecule was chosen.

4:45 PM GG9.4
Gold Nanoparticle Assembly Within Soft Linear Templates.
Robert G. Shimmmin, Lori K. Sanders, Gerard C.L. Wong and Paul V. Braun; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Gold nanoparticles, 2 nm in diameter, have been assembled along or within a variety of linear templates. To facilitate their assembly they have been chemically functionalized. The systems studied include quaternary ammonium modified gold, which assembles along the negatively charged, rodlike biomolecule actin; alkanethiol-coated gold, which assembles within the cylindrical hydrophobic domains found in the hexagonal-phase lyotropic liquid crystals produced by some water-amphiphile mixtures; and carboxyl-modified gold, which assembles within the cylindrical hydrophilic domains found in the inverse-hexagonal phase lyotropic liquid crystals produced by some water-oil-surfactant ternary mixtures. We have used small angle X-ray scattering to probe the structure of these templated gold nanoparticle assemblies, addressing issues such as the effect of the nanoparticles' presence on the template's structure, the inter-nanoparticle spacing along or within the linear template, and the ability to form close-packed nanoparticle arrays. In systems where the nanoparticle surface chemistry permits interparticle cross-linking, we have exposed the nanoparticle-doped templates to such cross-linking treatments, and we contrast the results of such experiments to the cross-linking of the same gold nanoparticles in unstructured solution.

SESSION GG10: Poster Session: Mesoscale Architectures from Nanounits: Assembly, Fabrication and Properties II
Chairs: Paul Braun, G. Ramanath and Mauricio Terrones
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

GG10.1
Mesoporous Carbon/Silica Composite with Alternating Carbon-Silica Layers Integrated at a Molecular-Scale in the Pore Wall. Jiebin Pang and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Mesoporous silica is of great interest for many applications. Functionalization of mesoporous silica, a process that imparts functionality to the pore surface or pore wall, is essential to convert the relatively inert silica into various functional materials. Up to date, functionalization of mesoporous silica is often achieved by post-grafting methods, direct synthesis methods, or by using functional surfactants. The direct synthesis method provides mesoporous silica with functionalities through co-assembling surfactants with organosilane precursors that contain non-hydrolyzable pendant or bridged organic ligands. However, current research in this area has been focused on the synthesis of functionalized mesoporous silica with organic or metallic moieties. This work reports the synthesis of ordered mesoporous carbon/silica composites with unique pore walls that are composed of molecularly integrated layers of silica and carbon. This is achieved by co-assembling octadecyltrimethylammonium bromide (OTAB) with 1,4-bis-(triethoxysilyl)benzene (BTEB), followed by a carbonization process that decomposes the surfactant and converts the phenylene moieties into carbon. The materials were characterized by X-ray diffraction (XRD), nitrogen and hydrogen sorption isotherms, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and other techniques. The incorporation of carbon layers into the pore wall not only results in interesting mesoporous carbon/silica

nanocomposites with meso- and molecular-scale order, but also may provide materials with improved thermal, chemical, and mechanical properties. Furthermore, removal of the silica from the carbon/silica nanocomposites results in mesoporous carbon with positively replicating mesostructure. Compared with the current two-step templating synthesis of mesoporous carbon, this method provides a direct method to synthesize ordered mesoporous carbon for hydrogen storage (e.g., 1.2 wt % at ambient pressure and 77 K), catalysts, fuel cells, and other applications.

GG10.2

Characterization of Polymeric Gratings Formed Under

Tensile Stresses. Leonard F. Pease¹, Paru Deshpande², Stephen Y. Chou² and William B. Russel¹; ¹Chemical Engineering, Princeton University, Princeton, New Jersey; ²Electrical Engineering, Princeton University, Princeton, New Jersey.

Recent experiments have shown arrays of polymeric ridges or gratings develop from thin films sandwiched between pairs of silicon or quartz wafers. The ridges form as the wafers separate under tensile forces. We will report on our efforts to characterize this process and the resulting gratings. The ridges only form below the bulk glass transition temperature; brittle polymers including polystyrene and poly(methyl methacrylate) may be used. Electron and atomic force microscopy indicate ridges on one substrate are complementary to and interlocking with those on the opposite substrate. The spacing and interdigitating morphology are independent of the molecular weight. The thickness of the film is the only parameter shown to affect the period; the period scales as four times this thickness. Thus far periods ranging from 200 nanometers up to four millimeters have been achieved. While the process is particularly simple several issues remain. We are currently working to understand what controls the orientation, the fraction of the wafer covered (currently from less than a tenth up to half), and what determines the location of lines that do form. We are also investigating the role of the interface in the development process. Such characterization is necessary before the resulting gratings can find application, which may eventually range from bioscaffolds, to templates for patterning of silicon, and microfluidics.

GG10.3

Hydrothermal Synthesis of TiO₂ Nanosheet by Surfactant-Assisted Hydrolysis of Titanium Alkoxide. Fumin Wang, Kyoto University, Kyoto, Japan.

This paper describes a novel method for preparation of TiO₂ nanosheet of quasi-anatase phase. By hydrolysing titanium isopropoxide in a surfactant-containing solution, quasi-anatase nanosheets have been synthesized by hydrothermal method at low temperature (140celsius degree). The structural features of the formed titanium oxide nanosheets were examined by scanning electron microscopy, transmission electron microscopy and electron diffraction analysis. The results are compared with those prepared by existing exfoliation process obtained from layered titanate. The prepared nanosheets by our method have a molecular thickness about 0.7 nm and high crystallinity. The electron diffraction pattern corresponds well with the 0.38 nm×0.30 nm periodicity structure, which reflects the two-dimensional atomic arrangement in the nanosheet. The titanium oxide nanosheets formed in this process often present as a multisheets structure with TiO₂ sheets sandwiched with the surfactant. By removing the surfactant and under the presence of some positive ions, the multisheets structure can be exfoliated into mono-nanosheet, which resulted in a stable colloidal suspension. The experimental results show that the ratio of surfactant to titanium is an important factor for formation of titanium oxide nanosheet. A threshold of this ratio for making TiO₂ nanosheets is determined by an adsorbing amount of surfactant that can cover the nanosheet surface sufficiently. The surfactant plays a role isolating the nanosheets and suppressing the crystallization from quasi-anatase to real anatase phase. After the removal of the surfactant from nanosheet galleries, reconstruction of nanosheet from quasi-anatase phase was promoted and the real anatase nanorods or sheets with nano-scale thickness can be formed as a preferred product in the hydrothermal process. The shape involvement in this process is also determined by the presence and concentration of some positive ions. Furthermore a plausible mechanism was proposed for the formation of quasi-anatase nanosheets in our system .

GG10.4

Observations of the formation of particulate assemblies from dispersions. Derek Malcolm Holmes, Luc Jean Vandeperre, R. Vasant Kumar and William John Clegg; Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

When the liquid is removed from a dispersion of sub-micron particles on a substrate, the in-plane shrinkage that would otherwise occur is constrained. This gives rise to a misfit strain between the particulate

layer and the substrate, which can cause cracking of the final body or deformation of the substrate. These effects are commonly interpreted in terms of a stress caused by capillary pressure that builds up as the liquid leaves. Observations of dispersions cast onto a silicon substrate show that formation of the solid body occurs by the horizontal passage of two fronts from the outside to the centre of the layer. To investigate the processes that occur as assembly takes place and the fronts pass through the dispersion, the through-thickness shrinkage was measured by laser extensometry. The results show that assembly of initially dispersed particles into a packed layer occurs at the first front, and that the second front is associated with further liquid loss from the packed body. This is consistent with previous results. An optical interferometry method was used to record deformation of the silicon substrates during assembly. These experiments show that the build up of deformation across the plane of the substrate is not uniform, and that the deformation is related to the localised misfit strain associated with the passage of the two fronts. The magnitude and distribution of the misfit strains and hence the properties of the packed assembly can be influenced by modifying properties of the dispersion, such as the interfacial energies and the particle volume fraction.

GG10.5

Self-Assembly Approaches to Organogel Construction.

David W. Britt, Harshil Dhruv and Matt Draper; Biological Eng., Utah State University, Logan, Utah.

The ability of fatty amines and fatty acids to spontaneously self-assemble to form gels in water / alcohol co-solvents was investigated as a means to construct highly networked mesoscale architectures having high surface areas for potential use in protein and whole cell sensing and separation processes. Gel architecture and mechanical properties could be dramatically varied through selection of alcohol (methanol, ethanol, or propanol). The ratio of water / alcohol was also systematically varied to optimize gel formation, which only occurred for mixed aqueous / organic solvents. Gel formation could be further enhanced by introducing lactose as a gelling agent to improve miscibility of the system, presumably through formation of hydrogen bond networks bridging the surfactant head-groups. Interestingly, lactose lowered the gelling temperature of the fatty acid system, while raising the gelling temperature of the fatty amine system.

GG10.6

Microspheres Prepared by Sonication-Induced Assembly of Mesoporous Silica Nanoparticles. Philippa Jill Meadows,

Alexander Kulak and Stephen Mann; Chemistry, University of Bristol, Bristol, United Kingdom.

The ability to control the arrangement of nanoparticle building blocks into higher-order three-dimensional structures is desired to fabricate new synthetic materials with advanced structures and functions. In this work we have explored the sonication-induced assembly of mesoporous MCM-41 silica nanoparticles to produce microspheres with different morphologies, functionalities and porosities. Initially, calcined MCM-41 nanoparticles with spherical and worm-like morphologies were employed and the resulting microstructures were investigated by scanning electron microscopy. SEM images showed the formation of solid spheres, 1-10µm in diameter, comprised of closely packed MCM nanoparticles. Furthermore, microsphere preparation was extended to include amino and thiol functionalized silica nanoparticles with similar results. Microspheres were formed when microlitre volumes of a concentrated suspension of nanoparticles were sonicated in a large volume of toluene at low temperature. The plausible mechanism involves the dispersion of water droplets in the oil phase, which then act as emulsion templates. The hydrophilic silica nanoparticles self-assemble in the aqueous phase and form solid spheres as a result of the dissolution of the water in toluene. In other parallel experiments, it was found that the introduction of cationic and anionic surfactants greatly influenced the structure of the resulting aggregates, in some cases creating perforations in the microspheres. These appeared as circular apertures on the surface and spherical cavities throughout the structure and were attributed to the presence of sub-micron sized oil droplets within the dispersed water drops, which are stabilised by the surfactant. Building blocks with a negatively charged surface such as thiol functionalised and calcined particles interacted with anionic SDS to yield microspheres with multiple perforations. However, using cationic CTAB led to raisin-like structures due to the charge mismatching, causing particles to remain at the water/oil interface forming a skin, which crumpled on dissolution of the water. Conversely, with amino functionalised particles, introduction of cationic CTAB gave solid microspheres with perforations since the protonation of some of the amine groups gave the particle surface a slight positive charge. This work highlights a simple route for fabrication of ordered aggregates of amine and thiol functionalised particles. Surfactants have been employed to produce perforations in the microspheres creating microparticles with porosity on two different length scales. Such microstructures may find

applications in separation science or serve as catalysts with nanoparticle properties in ordered, micron sized aggregates.

GG10.7

A Novel Mediator-Template Assembly Route Towards Size- and Shape-Controlled Nanoparticle Assemblies.

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The ultimate exploration of nanoparticles in nanoelectronics, information storage, quantum computation, and chemical/biological sensors will depend on the ability to precisely assemble nanoparticles in controllable sizes and shapes with well-defined interparticle spatial properties. This presentation focuses on our recent findings of an investigation in this direction focusing on mediator-template assembly via multidentate thioether ligands. We have developed an effective mediator-template assembly strategy that can assemble gold nanoparticles into three-dimensional assemblies of controllable sizes (40-300 nm) and shapes. This strategy explores novel size- and shape-driving forces exerted by tetraalkylammonium bromide templating shells and multidentate thioether mediators. The assembly processes have been characterized in-situ by spectrophotometric, dynamic light scattering, and x-ray diffraction techniques. The morphologies have been probed by atomic force microscopy and transmission electron microscopy. Potential applications of the nanoparticle assemblies in sensors, catalysis, and nanoelectronics will be also discussed.

GG10.8

Periodic Array Nanostructures Using Colloidal Particle Lithography.

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In this work, we demonstrated a new preparation method of nanostructures using the combination of periodic array surface patterns in self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) by two-dimensional (2D) crystalline structure of colloidal particles, selective atomic layer deposition (ALD), and chemical etching. Periodic array patterns of OTS - SAMs were prepared by immersing of the Si substrate with 2D crystallized colloidal particles in anhydrous toluene solutions containing OTS molecules. Size of the periodic array patterned holes in OTS - SAMs was estimated by simple geometrical calculation to be 45 nm, 59 nm, and 70 nm when SiO₂ colloidal particles of 200 nm, 346 nm, and 500 nm in diameter, respectively, and OTS - SAMs (estimated thickness of 2.5 nm) are used. Experimental results showed the size of about 51.6, 78.7, and 93.7 nm, respectively, by atomic force microscopy (AFM). The estimated pattern size was achieved through the removal of the confined liquid in capillary between the colloidal particle and the substrate. Selective deposition of TiO₂ by ALD onto the patterned OTS - SAMs as a passivation layer and selective etching of oxide by hydrofluoric acid allows to fabricate the periodic array of isolated nanostructures in sub - 100 nm scale. This novel process can serve as an alternative method to fabricate nanopatterns and nanostructures.

GG10.9

Low Temperature Coalescence of Colloidal Gold Multilayers to Form Conductive Films.

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Gold films were fabricated on glass and a flexible polyimide; Kapton; by a solution-based assembly process using linker molecules. The substrates are modified by an amine-terminated silane and subsequently dipped in colloidal gold solution. The multilayers were built up by dipping the gold coated substrate alternately in a solution of 1, 6-hexanedithiol and colloidal gold solution. The resistance of the films after the deposition of 10 bilayers was ca. 1 M Ω . The films were heated at 3 different temperatures; 120°C, 160°C, and 180°C for different lengths of time. The resistance of the films decreased dramatically with increasing time of heating, and after 12 h a lowest resistance of 40 Ω was obtained. The decrease in resistance took longer times at lower temperatures. X-ray photoelectron spectroscopy revealed a decrease in the intensity of the S 2p peak from the dithiol, with increasing time of heating. Atomic force microscope and scanning electron microscope images of the samples showed a coalescence of the gold colloids with heating, leading to increased conductivity. The coalescence occurs due to a thermal desorption or degradation of the dithiol linker molecule. The thermal desorption of thiols from gold

surfaces has been observed before, but not for multilayer film of gold particles. This method paves a way for low temperature thermistor type devices on flexible materials. Another potential application is the patterning of the films by lasers, by selective heating, to form regions of different resistances for use in flexible electronics.

GG10.10

Direct Synthesis of Mesoporous Carbon and its Functionalization.

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In recent years, there has been a great interest in the synthesis of mesoporous carbons because of their unique structures and properties. Various types of mesoporous carbon materials have been fabricated using a complicated templating synthesis method. This method allows precise pore-structure control through replicating the mesostructure of the silica templates. However, the complicated multi-step synthetic procedures hamper the practical applications of these mesoporous carbons. Surface functionalization is a fundamental method for the application of carbon materials in catalysis and environmental process. Although the modification of activated carbon and carbon nanotube is well known, the functionalization of mesoporous carbon materials has been less investigated. In this work, mesoporous carbon with high surface areas, large pore volumes, and narrow pore size distributions was synthesized using low-cost sucrose as carbon precursor by a simple one step sol-gel technique followed by carbonization and template removal. The pore diameter of the mesoporous carbon is about 2.2 nm and the surface area is larger than 2000 m²/g. In order to explore a suitable functionalization condition, the mesoporous carbon was chemically modified using HNO₃ with different concentrations followed by SOCl₂ treatment and then reacted with the chemicals with different functional groups. In this study, nitrogen, phosphorus-containing ligands and sulfur, nitrogen-containing groups were successfully introduced to the surface of mesoporous carbon materials. The materials were characterized by nitrogen sorption, TEM, FTIR and NMR. The functionalized mesoporous carbon materials may have potential applications in catalysis and environmental process, such as preparation of organometallic catalysts and selective adsorption of heavy metals.

GG10.11

Using Surface Forces to Create Nanoscale Electrochemical Junctions.

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The anticipated size reduction of electrochemical devices such as batteries, capacitors, electrochromics, and sensors down to the micro- and nanoscale can benefit greatly from device junctions that are "self-organizing" rather than requiring the deliberate deposition or insertion of electrolytic layers. In this work we study the use of surface forces such as the repulsive van der Waals force to form such junctions. We use measured thermodynamic and spectroscopic data to select relevant material systems. The materials selection process includes calculations using frequency-dependent optical properties to determine the sign and magnitude of the vdW interaction and other surface forces between dissimilar conductive solids such as metals, graphite and conductive oxides, separated by organic solvents or polymers. Atomic force microscopy (AFM) is used to measure the interaction between single particles and between particles and films. For the first time, repulsive vdW forces have been demonstrated between electronically conductive materials capable of forming device junctions. Cyclic voltammetry is used to characterize the stability of the junctions at potentials relative to devices such as capacitors and lithium ion batteries. This approach is expected to be applicable to nanoscale junctions formed between colloidal particles and films in a variety of device geometries.

GG10.12

Surfactant and Colloidal Silica-Templated Synthesis of Mesoporous TiO₂ Particles with Anatase Wall.

Zhiwang Wu, Jiebin Pang, Hongmei Luo and Yunfeng Lu; chemical and biomolecular engineering, tulane university, new orleans, Louisiana.

In the past decade, mesoporous TiO₂ has attracted more and more attention because of its wide applications in photocatalysis, solar cell, chemical sensors, etc. However, compared with the sol-gel chemistry of silicon alkoxide, combination of transition metals (TMs) sol-gel chemistry with templating approach is more difficult to master due to the fast sol-gel reactions of transition metal alkoxide. In this work, two templating approaches were applied to synthesize mesoporous TiO₂ particles. The results confirmed the feasibility of both approaches. The first one was using aerosol-assisted co-assembly technique. This was achieved by atomizing TiO₂ sols containing

homogenous TiO₂ precursor and colloidal silica template. During the aerosol process, solvent evaporating from the droplets enriched the non-volatile components and resulted in co-assembly of TiO₂, colloidal silica into spherical particles. Subsequent crystallization of TiO₂ and removal of colloidal silica resulted in mesoporous anatase TiO₂ particles. The second route to the synthesis of mesoporous TiO₂ was using one-step hydrothermal technique. TiO₂ precursor (TiCl₄) hydrolyzed in the presence of surfactant (e.g., F127) under hydrothermal condition in absolute ethanol, resulting in mesoscopic crystalline structure. Mesoporous anatase TiO₂ particles were obtained after subsequent removal of the surfactant by solvent extraction. Particles obtained from both approaches exhibited high surface areas and crystalline (anatase) structures based on nitrogen sorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD) characterizations. These mesoporous anatase particles are of great significance for photocatalysis and other applications.

GG10.13

Surface Sol-Gel Modification of Mesoporous Silica Materials with TiO₂ for Assembly of Ultra-Small Gold Nanoparticles.
Wenfu Yan, Bei Chen, Shannon Mark Mahurin, Edward W. Hagaman, Sheng Dai and Steven H. Overbury; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Since their discovery in 1992, silica-based mesoporous materials have attracted intense interest because of their potential applications in catalysis and separations. However, most applications of these mesoporous materials usually require functionalization of a relatively inactive silica surface through the reaction of a high density of silanol groups with desired organic or inorganic species even the fabrication of mesostructured non-siliceous solids has been extensively exploited. Herein, we applied a hydrolytic surface sol-gel process, a technique developed by Kunitake and coworkers to fabricate metal oxide thin films with thickness control to nanometer precision on a flat substrate, on the modification of the surface properties of mesoporous silica materials. This technique generally consists of two half reactions: (i) non-aqueous condensation of metal-alkoxide precursor molecules with surface hydroxyl groups and (ii) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxyls. The one-layer film growth is achieved by repetition of saturated adsorption of alkoxides and subsequent regeneration of a uniform hydroxyl surface. By using this layer-by-layer approach, one layer of a high- dielectric point oxide component titania (≈ 6.0) was introduced on the mesoporous silica (SBA-15) surfaces under an atomic-level thickness control and excellent uniformity to decrease the negative charges of silica surfaces. BET analysis indicates that the pore size distribution is decreased from 7.4 to 6.0 nm for the first cycle and 6.0 to 4.7 nm for the second cycle. The reduction of the mesopore size for each cycle should be about twice the single layer thickness. Accordingly, the effective single layer thickness is about 6-7 Å. The gold precursors were readily introduced via the deposition-precipitation method on the surfaces of the modified mesoporous materials. The subsequent reduction of the surface immobilized gold precursors with CO successfully led to gold nanoparticles assembled inside ordered mesopores. Z-contrast transmission electron microscopy (TEM) image of the resulting materials shows the tiny highly uniform bright spots (0.8-1.0 nm diameter) along the mesopore channels correspond to the gold nanoparticles. The activity of the gold catalysts for CO oxidation was characterized. Comparisons were made between the Au/monolayer TiO₂-SBA-15 with Au/commercial nanocrystalline titania support (Degussa P-25). Comparably high activities (i.e., achieving 50% CO conversion above about -40°C) were found for Au catalysts on untreated support. High temperature (300°C, 30 min) 8%O₂-He treatment dramatically decreased the activity of nanocrystalline TiO₂ supported catalysts, as the light-off curve shifted to high temperature. By contrast, the activity of the monolayer catalyst did not change significantly, achieving >50% conversion at -25°C.

GG10.14

Control of Molecular Orientation of Phthalocyanine Films by using Ultrathin 3,4,9,10-Perylene Tetracarboxylic Dianhydride Template Layers. Takeaki Sakurai, Shunsuke Kawai, Jo Shibata, Ryosuke Fukasawa and Katsuhiro Akimoto; Institute of Applied Physics, University of Tsukuba, Ibaraki, Japan.

The molecular orientation in thin films of organic semiconductors dominates optical and electrical properties, and the performance of organic semiconductor devices would greatly depend on the molecular orientation and regularities. Most of the organic semiconductor molecules, especially conjugated systems, tend to incline their molecular plane away from the several kinds of substrates surfaces such as glass and conductive oxides. It is important to develop a control technique of molecular orientation. In this work, we studied the effects of surface modification of glass substrate on the molecular orientation of phthalocyanine (H₂Pc) films. It is well established that the molecular orientation of 3,4,9,10-perylene tetracarboxylic

dianhydride (PTCDA) is parallel to the surface of glass substrates, therefore, the surface modification of the glass substrate was carried out by depositing ultra-thin PTCDA. H₂Pc and PTCDA films were deposited on glass (Corning 7059) substrates by organic molecular beam deposition (OMBD) method. After the growth of 1.5 nm-thick PTCDA template layers, H₂Pc was deposited on it at room temperature with the thickness of 200 nm. The molecular orientation and structural properties of these layers were analyzed by X-Ray Diffraction (XRD) which provide the lattice periodicity perpendicular to the surface, Grazing Incidence X-ray Diffraction (GIXD) which provide the lattice periodicity parallel to the surface and Infrared Reflection Absorption Spectroscopy (IR-RAS) measurements. In case of the deposition of H₂Pc films directly on the glass substrate, the diffraction peak appeared at $2\theta = 6.8^\circ$ measured by XRD with θ - 2θ mode, and at $2\theta\chi = 7.3^\circ$ and 27° by GIXD with ϕ - $2\theta\chi$ mode. The 27° peak represents the stacking direction of molecular plane of H₂Pc. Therefore, these results indicate that the molecular plane of H₂Pc takes a standing arrangement on glass surfaces consistent with the previous results. Then we tried the deposition of H₂Pc on PTCDA template layers. A clear diffraction peak measured by XRD was observed at 27° , and the peak at 6.8° that was observed in the H₂Pc direct deposition was disappeared. In the GIXD measurements, the diffraction peak at 27° was not observed. These results indicate the orientation of H₂Pc molecular plane turned to the parallel arrangement by the surface modification by PTCDA. In the IR-RAS measurements, moreover, the peak of C-H bending vibration at 740 cm^{-1} , which is allowed at parallel arrangement by IR-RAS selection rule, was enhanced remarkably in the H₂Pc on PTCDA structure. These results also indicate the orientation of H₂Pc molecular plane turned to the parallel arrangement. In conclusion, it is suggested that the molecular orientation is strongly affected by surface and can be controlled by a modification of the substrate surface.

GG10.15

Multilayer construction of mixed ligand-protected CdS nanoparticles through covalent bond-forming reaction.
Takaaki Tsuruoka, Kensuke Akamatsu and Hidemi Nawafune; Konan University, Kobe, Japan.

Ligand-protected nanoparticles consisting of semiconductor cores surrounded by organic monolayers have attracted considerable interest for applications in materials science and nanotechnology. The organic surroundings can provide stability and additional functionality to the nanoparticles. Thin films are of particular interest for the development of novel devices that utilize the specific characteristics of semiconductor nanoparticles. The development of a method that allows effective surface modification of semiconductor nanoparticles with diverse surface functionalities would be extremely beneficial for the development of electrical and optical devices using these semiconductor nanomaterials. In this study, we report an experimental investigation of surface chemical modifications of CdS nanoparticles in order to form mixed monolayer-protected nanoparticles, along with a covalent bonding-based layer-by-layer approach for the fabrication of nanocomposite films on glass substrates. CdS nanoparticles initially prepared using the reverse micelle method were used to modify nanoparticle surfaces with 1-decanethiol molecules by ligand exchange. Subsequently, 11-mercapto-1-undecanol was partially incorporated by a place exchange reaction, thereby providing stable, mixed monolayer-protected CdS nanoparticles. The reactivity of surface hydroxyl groups was verified by a reaction with isocyanate-bearing molecules that provide carbamate bonds in high yields at ambient temperature. The obtained mixed monolayer-protected nanoparticles were successfully immobilized on a glass substrate through a carbamate bond-forming reaction that could be further utilized for multilayer construction in a layer-by-layer fashion.

GG10.16

Architecture of Multi-Layered and Multi-Structured Mesoporous Silica Thin Films by Multi Spin Coating.
Ji-In Jung, Jae Young Bae and Byeong-Soo Bae; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea.

The mesoporous silica thin films with ordered pore structure are promising materials in such applications as sensor arrays, nanoreactors, electronic and photonic function devices, low-dielectric constant films, and hosts for large organic species. Mesoporous silica films with different pore sizes and structures were prepared by using cationic surfactants (DTACl and CTACl) or PEO-PPO-PEO triblock copolymers (Pluronic F68, P123, and F127) as surfactant structure directing agents with tetramethylorthosilicate as silica source. The mesoporous structures of thin films were controlled with the ratio of amphiphilic alkylhalide surfactant and tetraalkoxysilane. They were synthesized by an evaporation-induced self-assembly process and spin-coated on Si wafer. A cumulative heating procedure that evaporates excess solvents and decomposes surfactants produced

structurally stable mesoporous silica films. Mesoporous silica films with different pore sizes ranging from 2 to 10 nm and mesopore wall thickness ranging from 1 to 5 nm were prepared by using different surfactants. Through multi spin coating, we made multi-layered thick films of the same pore surface property or multi-layered and multi-structured mesoporous silica films with different pore surface property such as pore size, pore structure, and hydrophobicity of pore surface. Well-organized multi-layered and multi-structured mesoporous silica films with periodically varying layer properties are applicable for optoelectronic devices, sensors, functional coating, and biological surfaces. Upper layers of mesoporous silica films were well adhered without delamination on the bottom layers after calcination. Ordered mesoporous structures were formed on the preformed mesoporous silica films, regardless of the substrate or bottom layer. This multi-layered mesoporous silica films provide well-controlled and ordered porous multi-mesostructures where each layer is deposited by multi spin-on process. The orientational and structural characteristics of multi-layered and multi-structured mesoporous silica films was investigated by XRD, AFM, SEM, and TEM. Through TEM cross-sectional images, we confirmed that the hexagonal mesostructured and multilayered films with different pore sizes of 3.5 nm and 7 nm were formed. Also, the different hexagonal/cubic mesostructured and multilayered films with different pore sizes of 3.5 nm and 10 nm were confirmed by TEM.

GG10.17

Bimetallic Nanoparticles: Preparation using Phase Transfer Method and the Study of their Properties. Shwetha A. Shetty¹, Sampath S.², Kamanio Chattopadhyay¹ and Ravishankar Narayanan¹; ¹materials research centre, indian institute of science, Bangalore, India; ²department of inorganic and physical chemistry, indian institute of science, Bangalore, India.

Multi-metallic alloy nanoparticles show excellent catalytic, electronic and magnetic properties and synthesizing them is a field of extensive research. In the present work alloy nanoparticles were synthesized in a two phase liquid-liquid system by phase transfer method using alkanethiols as capping agents. The evolution of alloy particles during synthesis is studied using transmission electron microscopy (TEM) to see whether they form core/shell bimetallic or partially segregated alloy or pure alloy structures in the nanoscale. The rules that govern these bi-metallic particles to go into these kinds of structures in the nanoscale were tried to find out using the TEM study. The work also includes the study of the properties exhibited by these alloy nanoparticles.

GG10.18

Electrospinning of Functional Nanofibers as Aligned Arrays and Functional Architectures. Jesse Thomas McCann, Dan Li and Younan Xia; Department of Chemistry, University of Washington, Seattle, Washington.

Electrospinning has garnered much attention recently as it provides an inexpensive and simple way to manufacture large quantities of nanoscale fibers. This system is traditionally used to spin organic fibers due to the viscoelastic requirement of the solutions. We have recently extended this system to spin composite fibers. By co-spinning sol-gel precursors with a water-soluble polymer, we have been able to tune the viscoelastic properties of the solution and thus spin uniform composite fibers with excellent size control down to tens of nanometers. We have also fabricated uniaxially aligned arrays of nanofibers. These structures could be stacked into structures for device fabrication. In addition, we have also devised a new two-capillary spinneret that is simple and easily manufactured in the lab. The use of this spinneret has allowed for the fabrication of hollow nanofibers with a good degree of morphological control. This poster will cover all these aspects, with a focus on the fabrication of functional architectures relevant to various nanoscale devices.

GG10.19

Electric-Field Assisted Assembly of ZnO Nanowire to Fabricate Field Effect Transistors. Liang-Yih Chen, Hsiao-Chiu Hsu and Chau-Nan Hong; Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan.

An electric-field assisted assembly technique is used to align ZnO nanowires on the interdigit electrodes to study their electrical properties. ZnO nanowires were synthesized by both furnace and hydrothermal methods. The nanowires were deposited on the interdigit electrode structures and then aligned in the 10 μm -wide electrode gaps by using alternating electric fields at frequency between 500kHz and 5MHz with field strengths between 10^5 and 10^6 V/m. SEM analysis shown that the nanowires aligned parallel to the electric field lines and electrically contacted with gold electrodes. The alignment along the electric field was due to the polarization of ZnO nanowire. The dielectrophoretic behavior of ZnO nanowires in microelectrode arrays have been studied as a function of frequency

and applied field strength. The electrical characteristics of the nanowire thin-film transistors (NW-TFT) on the interdigit electrodes deposited on SiO₂/Si substrates are being measured. By using this low temperature assembly process, the NW-TFT can be produced on various substrates including plastics.

GG10.20

Actively Controlled Self-Assembly of Colloidal Crystals by Electrocapillary Effect. Chun-Wen Kuo, Jau-Ye Shiu and Peilin Chen; Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan.

Self-assembly is a commonly used strategy in synthesis and fabrication. 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 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 microchannel networks. Using this approach, we can not only selectively fabricate the colloidal crystals in the desired channels, but we can also build colloidal crystals with different optical properties in different channels or in the same channel. This method is not limited to the fabrication of colloidal crystals. In general, it can be configured to produce other novel functional materials using self-assembly process when it is integrated with more sophisticated microfluidic system.

GG10.21

Self-Assembly of Gold Nanoparticles on Nanometer-patterned Surface. Kunji Chen, Yongjun Zhang, Xinfan Huang, Guanqi Han and Liangcai Wu; Nanjing University, Nanjing, China.

The self-assembly processes of gold nanoparticles on nanometer-step-patterned Si surface and polished Si surface were investigated by the convective self-assembly method. The colloidal gold particles with diameter around 10nm were synthesized using a reduction of chloroauric acid (HAuCl₄) with trisodium citrate and tannic acid, and ligated by dodecanethiol. The convective self-assembly method was used to deposit the colloids dispersed in benzene onto the substrates. The substrates were dipped into the solution vertically at room temperature. As the solvent evaporates the gold nanoparticles were grown onto the substrates. SEM results showed that the configurations of the gold arrays depended on the surface morphology of the substrates. On the nanometer-step-patterned Si surface the nanoparticles assemble into parallel lines, and the distance between the neighbor lines is around 35nm. On the polished Si surface the nanoparticles formed compact domains. In each domain the particles are close-packed in a two-dimensional hexagonal superlattice and are separated by uniform distances. The pattern variation of the gold arrays is due to different surface characteristics of the substrates. On the nanometer-step-patterned Si surface the steps play a critical role in the self-assembly process of gold nanoparticles. And the capillary force from the steps drives the particles to line along the steps. Therefore the particles tend to self-assembly into one-dimensional line structures when the solvent evaporates. For the polished Si substrate there is a little difference. The particles formed two-dimensional hexagonal superlattice without the directional confinement.

GG10.22

Self-Assembly of Low-Dimensional Nanoparticle Structures. Jiajie Diao¹, Shuogang Huang¹ and Mark Reeves^{1,2}; ¹Department of Physics, George Washington University, Washington, District of Columbia; ²Code 6363, Naval Research Laboratory, Washington, District of Columbia.

Low-dimensional nanoparticle structures are synthesized by two techniques designed to favorably control the energetics of colloidal self-assembly. In the first technique, evaporation-driven colloidal deposition, a vertically positioned substrate is partially immersed in a nanoparticle suspension, subject to evaporation at room temperature and atmospheric pressure. The interfacial force within the meniscus region at the solid-liquid-air interface enhances the adhesion of the suspended nanoparticles to the substrate. In this geometry, the horizontal orientation of the meniscus results in the formation of a nanoparticle wire. Removing a small amount of the liquid will interrupt the deposition process and wire-formation will resume at a new location. Changing the timing and amount of each liquid withdrawal easily controls the width of and spacing between the wires. In a second technique, electrode writing, a sharp tungsten wire is pressed against the backside of a substrate floating on a

nanoparticle suspension, thereby imposing an localized ac field. Finite element calculations show that the electrode concentrates the electric field, leading to dielectrophoresis just below the placement of the tip. The tip is then moved horizontally across the substrate as nanoparticles are deposited following its motion. In this way, low-dimensional nanoparticle structures are written on the substrate. The structure of the resulting films is characterized by scanning electron microscopy and atomic force microscopy and this reveals that the deposited material forms 1D, 2D, and fractal structures. We also characterize by resistivity measurements the electrical properties of metallic nanoparticle films formed by these techniques. We anticipate that electrical interconnects can be formed between planar circuit elements using these deposition approaches.

GG10.23

Oriented Attachment Growth of BaTiO₃ Nanoparticles. Songhak Yoon¹, Namsoo Shin² and Sunggi Baik¹; ¹Materials Science and Engineering, POSTECH, Pohang, South Korea; ²Pohang Accelerator Laboratory, POSTECH, Pohang, South Korea.

BaTiO₃ nanoparticles are synthesized under N₂ atmosphere at low temperature (<80°C) by the hydrolysis and condensation of barium hydroxide hydrate and titanium (IV) isopropoxide. It was found that synthesized primary particles were aggregates of nanosize nuclei. The binding of hydroxyl ion or water in nuclei leads to the oriented aggregating attachment resulting in primary nanoparticles of a few tens to hundred nanometers. Adjacent BaTiO₃ nuclei aggregate to share a common crystallographic orientation and subsequently to eliminate high energy surfaces. The size and shape of the aggregates varied depending on the reaction temperature, molar concentrations of precursors, and amounts of water added in the solution. Electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) were used for composition analysis and X-ray diffraction (XRD) for structural analysis of nanoparticles. Morphology development of nanocrystals has been characterized by means of high resolution transmission electron microscopy (HRTEM). Oriented Attachment is a dominant mechanism in early stage of crystal growth and subsequent microstructural development of BaTiO₃ nanoparticles.

GG10.24

Thermal and Mechanical Properties of PMMA/Silica Nanocomposites with Controlled Nanoparticle/Polymer Interfaces. Sarah L. Lewis¹, Robert G. Shimmin², Chunzhao Li³, Paul V. Braun², Brian C. Benicewicz³ and Linda S. Schadler¹; ¹Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ³Chemistry, Rensselaer Polytechnic Institute, Troy, New York.

Previous work with PMMA/alumina nanocomposites has indicated that both the filler size and the nature of the nanoparticle/polymer interface are important in determining the thermal and mechanical properties of the composite. A poor interface between the filler and matrix resulted in an order of magnitude improvement in ductility and a 20 degree decrease in glass transition temperature. The nanoparticles used in this study showed a broad size distribution and it was hypothesized that the large interfacial area provided by the smaller particles caused the decrease in glass transition temperature whilst void growth around the larger particles resulted in a change in failure mechanism from crazing to shear yielding. To test this hypothesis PMMA/silica nanocomposites were made by an in-situ polymerization method using monodisperse nanoparticles whose surfaces had been treated such that control over the polymer/nanoparticle interface was obtained. Composites were made using 15 and 150 nm monodisperse nanoparticles with fluorinated or methylated surfaces. This paper will report on change in ductility and glass transition temperature in these well-controlled samples. Initial results confirm the decrease in glass transition temperature in the composites with small particles, but not in those with large particles.

GG10.25

The Synthesis of Nanoporous Hydrogels Using Sacrificial Block Copolymers. Jungmee Kang and Kenneth J. Beers; Massachusetts Institute of Technology, Cambridge, Massachusetts.

A means will be presented to produce nanoporous hydrogels through block copolymer templating. Micellar solutions of block copolymers of poly(ethylene oxide) (PEO) and a degradable component are cross-linked in an electron beam to produce hydrogels. Degradation of the labile blocks opens pores in the gel that reflect the microstructure of the ordered micelle phase. SAXS and SEM studies of these materials before and after degradation show order on the scale of 10-100 nm. The chemical means to produce these hydrogels will be presented, along with studies of the effect of cross-linking conditions on hydrogel properties and mass-retention during degradation of the labile blocks. Experimental results suggest that macromolecular diffusion through the hydrogel should be less than an order of

magnitude of that through the pores, opening possibilities for selective or responsive macromolecular transport in these gels. The resulting nanoporous PEO hydrogels should have chemical functionality in the pore-bounding regions that provides a means to further chemical modification. In addition to experimental results, field-theoretic calculations of the block copolymer micelle structure will be discussed.

GG10.26

Synthesis, Characteristics, and Applications of Polypyrrole and Poly(3,4-ethylenedioxythiophene) Nanotubes and Nanowires. Bohyun Kim¹, D. H. Park¹, D. S. Sub¹, S. J. Lee¹, H. M. Kim¹, Jinsoo Joo¹, Haeyong Kang² and Won Kang²; ¹Physics, Korea University, Seoul, South Korea; ²physics, Ewhawomans University, Seoul, South Korea.

Nanotubes and nanowires of π -conjugated polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized by using nanoporous template through electrochemical polymerization method. Dodecylbenzenesulfonic (DBSA) acid or tetrabutylammonium hexa-fluorophosphate (TBAPF₆) were used as dopant in electrolyte. Either a HF or NaOH solution was used to remove the aluminum oxide template after polymerization. From the TEM and SEM photographs, we observed the formation of tube with diameter of 50 nm to 200 nm, length of 50 nm, and wall thickness of 20 nm. The formation of tube or wire and the length including diameter of the systems were determined by the synthetic conditions, such as applied current, doping level, and polymerization time. The dc conductivity (σ_{dc}) of one strand of PPy-TBAPF₆ nanotube treated HF dissolving solvent was measured to be 2×10^{-1} S/cm by using four-probe method, while that treated with NaOH dissolving solvent was 4×10^{-3} S/cm. The σ_{dc} of PEDOT-DBSA nanotubes treated with HF solvent was 10 S/cm, while that treated with NaOH solvent was 2×10^{-4} S/cm. The electrical properties varied with the use of different dissolving solvents to remove the template. The sdc and I-V characteristics as a function of temperature were measured on photolithography pattern from 300 K to 0.3 K. The UV/Vis absorbance and FT-IR spectra of the nano-systems were measured for the optical and structural properties. We observed the dramatic increase of field emission (FE) current by using these nanotubes or nanowires for the nanotip emitters for FE, implying the promising nano materials for FED.

GG10.27

Controlled PMMA Particles Assembly on Substrate by Synchrotron X-ray Using Dispersion Polymerization. Jin Xiao¹, Jae-Mok Yi¹, Seong Kwon Seol¹, Jung Ho Je¹, Yung-Chin Yang² and Yeukuang Hwu²; ¹Materials Science and Engineering, Pohang University of Science and Technology, Pohang, South Korea; ²Institute of Physics, Academia Sinica, Taipei, Taiwan.

Controlled assembly of micro or nano sized polymer particles on substrate has a potential to be applied to micro electrical and mechanical devices. However, it is not easy to control assembly of particles in a manner of diverse size and/or density and further to specific local areas. In this work we first tried to fabricate the poly methyl methacrylate (PMMA) particles assembly on various substrates using synchrotron x-ray induced dispersion polymerization. Depending on the x-ray flux exposed on substrates which were immersed in the dispersion media, the size and/or density of the PMMA particles were able to be controlled on selective areas. Interestingly the growth of the PMMA particles was hindered on specific areas of substrates which were exposed with higher x-ray flux, resulting in lower size and/or density of the PMMA particles. Such obstruction effect on areas with higher flux was attributed to a negative potential barrier layer that might be formed by concentration gradient of hydrated electrons, which can be generated by the irradiation of x-rays on substrates in the solution. Based on the obstruction effect in higher flux zone, we were able to fabricate a well defined assembly of PMMA particles in a manner of diverse size and/or density just by using a patterned mask for controlling the x-ray flux.

GG10.28

Nanocrystal-doped polymer spheres as building blocks for coupled resonator optical waveguides. Bjoern Moeller¹, Nicolas LeThomas¹, Mikhail Artemyev² and Ulrike K. Woggon¹; ¹Physics, University Dortmund, Dortmund, Germany; ²Institute for Physico-Chemical Problems, Belarussian State University, Minsk, Belarus.

Colloidal CdSe nanorods (NR) and nanodots (QD) are nanoemitters that received much attention in recent years. NRs, for example, emit highly polarized light and can be used as active optical material in laser devices and photonic structures. In this contribution we study CdSe-doped microspheres of radii $R \approx 2\lambda$ as building blocks for coupled resonator optical waveguides. Unlike other types of optical waveguides, waveguiding in the coupled-resonator optical waveguide

(CROW) is achieved through weak coupling between otherwise localized high-Q optical cavities [1]. This new type of waveguiding might replace waveguiding by total internal reflection and waveguiding through Bragg reflection from a periodic structure. The coupled microsphere cavities were prepared by impregnating polystyrene microspheres with a subsurface layer of CdSe nanocrystals [2,3]. To achieve coherent photon coupling, exactly size-matched microspheres (<0.1% size deviation) have been pre-selected via their Mie resonances. The coupled cavities, arranged in linear chain or various two-dimensional geometries (photonic molecules) are studied by micro-photoluminescence spectroscopy at the diffraction limit combined with polarization sensitive mode mapping. The spatial distribution and the dominant polarization type of both the weakly and strongly coupled cavity resonances excited by the nanocrystal emission are studied spectrally and spatially. We demonstrate that a nanocrystal positioned on an equatorial plane of a photonic molecule results in a weak coupling with no significant loss in the Q-factor while a nanocrystal on the bi-sphere axis excites strongly coupled bi-sphere modes with strong field concentration in three points along the bi-sphere axis. Both experiment and theory show strong photon mode coupling with pronounced mode splitting as well as weak coupling with no significant loss in Q-factor depending on the emitter position and orientation. We show for the first time a three-resonator coupling without Q-factor degrading. [1] A. Yariv, Yong Xu, R. K. Lee, A. Scherer, Opt. Lett. 24, 711 (1999). [2] U. Woggon, R. Wannemacher, M. V. Artemyev, B. Moeller, N. LeThomas, V. Anikeev, O. Schoeps, Appl. Phys. B 77, 469 (2003). [3] B. Moeller, U. Woggon, M. V. Artemyev, R. Wannemacher, Appl. Phys. Lett. 83, 2686 (2003).

GG10.29

Electrostatic Assembly in Aerosol-Processing; Tailoring the Energy Release Rate of NanoEnergetic Materials.

Soo H. Kim^{1,2} and Michael R. Zachariah^{1,2}; ¹Mechanical Engineering, University of Maryland, College Park, Maryland; ²Physics, National Institute of Standards and Technology, Gaithersburg, Maryland.

Nanostructured fuel/oxidizer composites are being looked upon as a possible approach to enhance energy release rates. We have developed a new method for the formation of energetic nanocomposite aerosol materials, composed of assembled fuel and metal oxide nanoparticles with significantly higher energy release rate. The method is based on electrostatically enhanced assembly to promote the preferential arrangement of aluminum (fuel) nanoparticles with iron oxide (oxidizer) nanoparticles in the aerosol phase. Two unipolar chargers are employed to generate oppositely charged aluminum and iron oxide particles, which enhance the formation of intimately interconnected nanocomposite energetic materials. The results of TEM and STEM elemental mapping analysis indicates that the negatively charged aluminum nanoparticles are homogeneously distributed around positively charged iron oxide nanoparticles. The results of burning tests and thermal analysis using differential scanning calorimetry (DSC) showed that aluminum/iron oxide nanocomposite aerosol materials synthesized by electrostatic assembly had burning rates that are a factor of 10 higher than those produced by random Brownian coagulation.

GG10.30

Shape-controlled Synthesis and Orientation-ordered Superlattices of Spinel Ferrites Nanocrystals. Qing Song and Z. John Zhang; School Of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

The current intense researches on nanomaterials have been conducted due to their novel electronic, optical, magnetic, thermal, and mechanical properties. Recently, keen interests have been expanded into controlling the shape of nanomaterials and understanding the correlations between the material properties and its shape. The shape of nanomaterials can be as vital as the size in determining the uniqueness and novelty of material properties. Moreover, the assembly of nanometer unit building blocks is a key process in the design and construction of devices, and the shape of nano-building blocks and related properties will be crucial for such assembly and device designs. Shape-controlled synthesis of nanocrystals is an experimental challenge. Successes in shape control of nanocrystals have been reported in the syntheses of metals and semiconductors. Certainly, it is desirable to develop strategies for shape-controlled syntheses of complex metal oxides possessing rich properties, especially the magnetic characteristics. Here we present the combination of non-hydrolysis with seed-mediated growth in size and shape-controlled synthesis of complex metal oxides nanocrystals as well as the role of nanocrystalline shapes on magnetic properties and the determination of orientation-ordered superstructures formed by shaped nanocrystals of spinel ferrites. First part is concentrated on the shape-control of monodispersed spinel cobalt ferrite, CoFe₂O₄ nanocrystals, which shows a highly reversible shape evolution between a nearly spherical shape and an almost perfect cube. Moreover, the magnetic studies on such cubic CoFe₂O₄ nanocrystals indicate that

the blocking temperature, saturation and remnant magnetization of nanocrystals are solely determined by the volumes (sizes) of nanocrystals regardless their shapes. However, the shape of nanocrystals is a dominating factor for the coercivity of nanocrystals. In second part, magnetite, Fe₃O₄ nanocrystals with truncated tetrahedral platelets (TTP), tetrahedral platelets (TP), truncated octahedral (TO) and octahedral (OT) shapes have been observed in seed-mediated growth process. Transmission electron microscopy (TEM) analysis indicates that the nanocrystals in each shape tend to selectively accumulate together to form orientation-ordered superlattice assemblies. The accumulations of the Fe₃O₄ nanocrystals in shapes of TTP, TO and OT show hexagonal, primitive cubic, and distorted body center cubic (bcc) superlattice structures, respectively. Such magnetic nanocrystals with distinct shapes and their highly orientation-ordered shape-selective self-assemblies of magnetic nanocrystals possess tremendous potentials in fundamental understanding of magnetism and in technological applications of magnetic nanocrystals for high-density information storage.

GG10.31

X-ray Reflectivity and EXAFS Studies for Gold and Palladium Nanoparticles.

Yuan Sun¹, A. Frenkel², C. Shonbrun³, M. Fourman³, R. Isseroff², Y. Seo⁴, T. Koga¹, Nan-Loh Yang¹, Miriam H. Rafailovich¹ and Jonathan C. Sokolov¹; ¹Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York; ²Physics, Stern College, New York, New York; ³Stella K Abraham High School, Hewlett, New York; ⁴Center for Neutron Research, NIST, Gaithersburg, Maryland; ⁵Chemistry, College of Staten Island of the City University of New York, Staten Island, New York.

We have investigated the differences between the alkanethiolate Au and Pd nanoparticles synthesized by 1-phase(1) and 2-phase(2) methods with a metal/thiol ratio of 1:1, 1:2, 2:1, and 3:1. In order to understand the particle structure and chemistry, they were analyzed by several complementary techniques. The particles were deposited at the air-water interface in a Langmuir trough. However it was found that only the particles synthesized with 2-phase method spread at the water surface. These films were lifted onto TEM grids and Si wafers, and then studied by TEM and X-ray reflectivity (XR). XR performed on beamline X10B of the BNL/NSLS indicated that the thickness of the particle cores was smaller than the TEM mean size, which would indicate that the particles assume an oblate shape when exposed to water. Since both the thiol shell and the spreading solvent are very hydrophobic, it is not clear why the nanoparticles would spread on water. We therefore proposed that tetraoctylammonium bromide (TOABr) absorbed during synthesis might act as the hydrophilic headgroups in the 2-phase particles and helped them spread. The lack of TOABr on surfaces of 1-phase particles prevented the successful spreading of these particles. EXAFS, XR, TGA and XRD measurements were performed on the particles. The thiol coverage determined from EXAFS, XR, and TGA analysis indicated that there were about 237 and 70 thiol chains per particle for 1- and 2-phase Au particles, respectively. By modeling the EXAFS results we obtained that they were consistent with a cuboctahedral motif with diameter of 8.6 and 14.3 angstroms for 1- and 2-phase Au particles, respectively. These values are significantly smaller than those measured with TEM. It was therefore postulated that this may be due to structural disorder in the case of Au and possibly unbound reaction products in the Pd case. EXAFS examination for LB film of 2-phase Pd particles also confirmed their oblate shape, which was in good agreement with XR and TEM measurements. EPR was also used to determine whether any of the particles was magnetic. The data indicated only the 2-phase Pd particles had a sizable magnetic moment. +Supported by NSF-MRSEC program References (1) Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; Rafailovich, M.; Sokolov, J. Langmuir 1999, 15, 3486. (2) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, J.; Whyman, R. J. Chem. Soc., Chem. Commun., 1994, 801.

GG10.32

Thermal stability and enhanced interfacial adhesion of Cu-capped self-assembled molecular nanolayer barriers on SiO₂. Darshan D. Gandhi, P. G. Ganesan and G. Ramanath; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Sustenance of continual miniaturization below 45-nm feature sizes in micro-devices requires the use of nanometer-thick uniform barrier layers to inhibit Cu transport into adjacent dielectric material, and enhance interfacial adhesion. Self-assembled molecular layers (SAMs) with chosen terminal groups and lengths provide an attractive alternative to refractory metal/compound layers formed by conventional or emerging deposition techniques^{1,2,3}. The ability of SAMs to withstand the processing temperatures (450 °C) during device fabrication, and or operation, however is a concern. Studying Cu-capped SAM structures is of particular relevance because during device fabrication the SAMs, if used as diffusion barriers, are not

expected to be directly exposed to vacuum or air at high temperatures. Here, we report the thermal stability of Cu-capped SH-terminated SAMs of 3-Mercaptopropyltrimethoxysilane [MPTMS: (HS-(CH₂)₃-Si-(OCH₃)₃)] and the effect of vacuum annealing on the interfacial adhesion measured by 4-point bend tests. Cu/MPTMS/SiO₂ structures annealed to 700 °C show factor-of-9 higher interfacial debonding energies compared with reference Cu/SiO₂ samples heated to the same temperature. X-ray photoelectron spectroscopy (XPS) of fracture surfaces reveal that enhanced a) interaction between Cu and SH groups and b) siloxane bond formation at the MPTMS/SiO₂ interface are the adhesion enhancement mechanisms. At temperatures <400 °C, the concentration of siloxane bonds between the MPTMS and SiO₂ is low, leading to low debonding values. This is consistent with a high Si 2p/S 2p intensity ratio of 4.5, obtained by XPS spectra from the Cu fracture surface. At higher temperatures, the ratio drops to 1 indicating fracture at SiO₂-MPTMS interface. Our results indicate that Cu-capped SAM layers may meet the thermal stability requirement for incorporating in future interconnect structures. References: ¹ A. Krishnamoorthy, K. Chanda, S. P. Murarka, and G. Ramanath, J. G. Ryan, *Applied Physics Letters*, 78, 2467 (2001). ² P.G. Ganesan, J. Gamba, A. Ellis, R.S. Kane and G. Ramanath, *Applied Physics Letters*, 83, 3302 (2003). ³ P.G. Ganesan, A.P. Singh, G. Ramanath, *Applied Physics Letters*, Article in press.

GG10.33

Engineered Metalodielectric Nanostructures for Novel Sensing Applications. Sarah M. Emmons¹ and Miriam Deutsch²; ¹Chemistry, University of Oregon, Eugene, Oregon; ²Physics, University of Oregon, Eugene, Oregon.

The synthesis and characterization of nano- and meso-structured materials capable of detecting changes in their environment with ultra high sensitivities have been receiving much attention over the recent years. There are many challenges for the realization of these systems, such as identifying the underlying physical principles defining the sensitivity limits of given sensor architectures, understanding the operational capabilities of specific materials or structures, and the development and characterization of new materials for integrated nano-sensors. We present here the synthesis and characterization of new metalodielectric core/shell particles suitable for various sensing applications. Silver nanoshells with controlled grain size and thicknesses deposit uniformly on the surfaces of sub-micron silica spheres via a modified Tollen's reaction. The metal-coated spheres are subsequently pressed into pellets, while the electrical resistance of the composite is monitored. Alternately, ordered opaline structures may be formed via colloidal self-assembly, utilizing the core/shell particles as elemental building blocks. A clear advantage of these metalodielectric structures is that the amount of metal present is determined by the metal shell size and morphology, and not by the complete filling of interstices. The nanoshell structure, which is important for optimizing sensor performance, may in turn be independently engineered through the chemical deposition protocol. Thus we maintain control of the nanoshells' composition and morphology, and additionally of the structure of the final composite. Various sensing capabilities may be achieved through optical and electrical responses of the assembled materials. We will discuss in particular the electrical resistance of assembled structures with different shell morphologies, as functions of pressure and sphere-disorder. Structural characterization of the shells will be presented, and their suitability for applications such as pressure and humidity sensing will be addressed.

GG10.34

Fabrication of Ideally Ordered Metal Hole-Array Membranes Based on Anodic Porous Alumina and Their Optical Properties. Kazuyuki Nishio^{1,2} and Hideki Masuda^{1,2}; ¹Department of Applied Chemistry, Tokyo Metropolitan University, Tokyo, Japan; ²CREST, JST, Saitama, Japan.

The fabrication of ordered nanohole arrays is of growing importance for preparing various types of nanometer-scale devices. For preparing the nanohole arrays, process based on self-organization is promising because it yields ordered fine structures over large areas, which is difficult to achieve with conventional lithographic techniques. Anodic porous alumina, which is formed by anodization of Al in appropriate acid solutions, is a typical self-organized structure with uniformly sized holes. Porous alumina is useful as a starting structure for the fabrication of several kinds of devices because of its ordered hole-array structure with high aspect ratio.[1] Here, we report the fabrication of ideally ordered metal hole arrays using anodic porous alumina and their optical properties. Ideally ordered hole configuration enables us to study optical properties caused by interactions between the hole-array structure and wavelength of the incident light. Ideally ordered metal hole arrays were prepared by two-step molding process using ideally ordered anodic porous alumina as a starting material. In this process, the fabrication of negative-type of anodic porous alumina

and the subsequent formation of the positive type generate hole arrays of other materials than alumina with a geometrical structure identical to that of the original porous alumina.[2] We fabricated ideally ordered Ni, Au and Ag hole-array membranes by changing the solutions for electroforming.[3] The size and interval of the holes of the metal hole-array membranes were precisely controlled by changing those of the original porous alumina, and the depth of the holes was controlled by adjusting electroforming time. The transmission spectra of the metal hole-array membranes with submicrometer dimensions showed a highpass characteristic in the visible range, and cut off wavelength was dependent on the hole size. The optical property of metal hole array was also dependent on the refractive index of the medium in the holes. The wavelength at the peak in the transmission spectrum linearly increased with increasing the refractive index of the medium in the holes. This result indicates that the refractive index of the medium in the holes can be detected based on the optical property of the ideally ordered metal hole array. Ideally ordered metal hole-array membranes will be used in the fabrication of several types of optical device. Furthermore, they will be useful in the spectro-electrochemical analysis in solutions. 1. H. Masuda and K. Fukuda, *Science*, 268, 1466 (1995). 2. K. Nishio, M. Nakao, A. Yokoo and H. Masuda, *Jpn. J. Appl. Phys.*, 42, L83 (2003). 3. K. Nishio and H. Masuda, submitted.

GG10.35

Characterization of Mesoporous Silica Nanoparticles and Their Application for Low Refractive Index Materials. Tsuneo Yanagisawa¹, Takao Hirokado¹, Ryouzuke Nakamura¹, Kazuyuki Kuroda² and Tooru Kinoshita¹; ¹Advanced Material Research Group, Sumitomo Osaka Cement Co., Ltd., Funabashi-shi, Chiba, Japan; ²School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo, Japan.

Mesoporous silica particles are expected to be useful for catalysis supports and adsorbents because of their mesoporosity. On the other hand, the density and refractive indices of bulk materials can be controlled by involving mesoporous silica particles because air can be introduced with these particles. Also, transparency of bulk material can be kept when mesoporous silica particles were finely ground in order not to scatter visible light and uniformly dispersed into bulk materials. In this presentation, mesoporous silica nanoparticles synthesized by our company were characterized and applied for low refractive index materials. Our mesoporous silica nanoparticles have ca.30nm in particle size, ca.2nm in pore diameter, 1000m²/g of specific surface area. The refractive index of the particles was estimated to be 1.27. We applied the mesoporous silica nanoparticles to form single layered anti-reflection films. The refractive index of the films containing the mesoporous silica particles became lower reverse-proportionally with the amount of the particles in films. Hence it was confirmed that the mesopores in particles worked effectively to control the refractive index of the films. Also the surface of these mesoporous silica nanoparticles was modified with bulky organic groups to stopper the pores in the particles. Thus these modified particles were not penetrated by solvent or binder molecules. Films were formed with dispersed modified mesoporous silica nanoparticles and binders. These films showed characteristic values available to a single layered anti-reflection film (the transfer ratio of total visible light = 94%, the lowest reflection ratio = 0.5%).

GG10.36

Sensitivity of Self-Assembled Gold/Alkanedithiol Films to External Hydrostatic Pressure. Keith Higginson, Triton Systems, Inc, Chelmsford, Massachusetts.

The response to external hydrostatic pressure of self-assembled multilayer films of gold nanoparticles was investigated in an effort to develop a sensitive, non-intrusive technique to measure hydrostatic pressure at surfaces, similar in function to pressure-sensitive paint, but functional in underwater environments. Gold nanoparticles were initially deposited on thiolated substrates, and alternating layers of hexanedithiol or decanedithiol "spacer" molecules and gold particles were sequentially deposited to create self-assembled films up to ten layers thick. A broadening and red shift in the plasmon resonance band was observed as the interaction distance between the particles was changed on compression. Hydrostatic pressures in the range of hundreds of psi could be measured in this fashion.

GG10.37

Gate Modulation Induced by Field Effects Using Self-Assembled Monolayer-Based Structures at Room Temperature. Dong-un Jin¹, Christos G. Takoudis¹, Jie Zhang²,

Paul Brazis² and Dan Gamota²; ¹Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois; ²Motorola Advanced Technology Center, Schaumburg, Illinois.

This study demonstrates that the ionization at the end groups of Self Assembled Monolayers (SAMs) due to the application of an electric

field results in gate modulation. The observed gate modulation is achieved using bottom gate type three-layered devices, without a semiconductor layer. Electroless plated copper has been used for the bottom gate to realize high adsorption and orientation of SAMs in order to mitigate the occurrence of high leakage currents. Copper ions (Cu^{2+}) generated during the electroless plating process appear to act as channels in these field effect devices. In contrast to typical molecular devices using scanning tunneling microscopy or atomic force microscopy, the field effect devices in this work have been fabricated using simple methods. Also, these devices were operated with large effective contact areas ($\sim 2 \text{ mm}^2$) between the SAMs and metal electrodes at room temperature. The results of this study suggest that molecular devices designed with large contact areas and fabricated by simple electroless plating processes could provide a new device platform for several future applications.

GG10.38

Ordered Nanostructures for Organic Photovoltaic Cells. Vignesh Gowrishankar and Michael McGehee; Materials Science, Stanford University, Stanford, California.

The most common strategy for making organic photovoltaic cells efficient is to use a bulk heterojunction in which excitons are split at an interface between two semiconductors with offset energy levels. Since excitons only diffuse 4-20 nanometers in most organic semiconductors before they decay, the semiconductors must be patterned at this length scale. An ideal bulk heterojunction consists of a 100 to 300-nm thick film of one semiconductor with arrays of 10-50-nm wide pores filled with another semiconductor. We will show that the arrays of pores can be made in thin films of silicon or titania using Nanosphere Lithography and Block Copolymer Lithography along with reactive ion etching. The pores can be filled with conjugated polymers by melt infiltration or electropolymerization. The charge carrier mobility of the polymer inside the pores is almost one hundred times higher than that in normal films of just the polymer because the chains align along the straight pore walls. Photoluminescence quenching experiments show that excitons formed in the polymer are efficiently split by electron transfer at the organic-inorganic interface.

GG10.39

Effect of Restructuring, Metal Loading and Catalysis Reaction on Nanoporous Carbon. Ponnaiyan Ayyappan and Henry C. Foley; Chemical engineering, Penn State University, University Park, Pennsylvania.

The synthesis of nanocarbon materials is typically done with high energy processes including the use of high powered arcs and lasers for graphite vaporization. Recently, progress has been made in the catalytic synthesis of single and multiwalled nanotubes using gaseous precursors and transition metal nanoparticles to produce CNTs. Temperatures in such reactions are still high and control of the product in terms of selectivity is low. These factors motivate the exploration of new approaches the synthesis of carbon materials with nanoscale features at even lower temperatures. Such approaches to solids synthesis are called soft-chemical processes and offer the promise of rational and directed synthesis. In this poster we present an unprecedented solid state transformation of amorphous carbon to graphitic carbon due the metal addition. We also like to emphasize the effect of alkali and transition metals addition and gas phase catalytic reaction on the nanoporous carbon.

GG10.40

Possible Superconductivity in Langmuir-Blodgett Films based on Dialkyldimethylammonium-Au(dmit)₂ salts. Yasuhiro F. Miura¹, Shin-ichi Morita¹, Ryo Watanabe¹, Michio Sugi¹, Masato Hedo² and Yoshiya Uwatoko²; ¹Department of Functional Chemistry, Toin University of Yokohama, Yokohama, Kanagawa Prefecture, Japan; ²Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba Prefecture, Japan.

Fabrication of a superconducting Langmuir-Blodgett (LB) film is one of the long-standing goals among various trials for fabricating LB films with electronic and opto-electronic functions. Since the LB technique allows us to transfer two-dimensional (2D) molecular sheets from the air/water interface onto solid supports and fabricate tailored mono- and multi-layered structures, the realization of superconductivity will open up the possibility for a variety of applications in the future. We have already reported that the ditetradecyldimethylammonium-Au(dmit)₂ (2C₁₄-Au(dmit)₂) shows an in-plane conductivity of 40-50 S/cm at room temperature with a metallic temperature dependence in the range 230-300 K [1] and that the ac magnetic susceptibility suggests the existence of the Meissner state below 4 K [2]. However, the resistance drop upon cooling is not seen for the sample batches of majority in the measurement down to 1.2 K

[3]. In this paper, we report that the hydrostatic pressure induces the resistance decrease on cooling as for the 2C₁₄-Au(dmit)₂ LB films. The 2C₁₄-Au(dmit)₂ salt was synthesized following the procedure of Steimecke et al. [4] and spread at the air/water interface using a 1:1 mixture of acetonitrile and benzene. The horizontal lifting method was utilized and the 2C₁₄-Au(dmit)₂ film at the air/water interface was transferred onto a 0.1-mm-thick poly(ethyleneterephthalate) (PET) sheet. The as-deposited LB film was rendered to be conductive by an electrochemical oxidation [1-3] and the resistance was measured along the film plane by an ac four-probe method in the temperature range 0.5-290 K. A hydrocarbon oil (Daphne Oil 7373, Idemitsu, Co. Ltd.) was used as the pressure medium. The resistance of the 2C₁₄-Au(dmit)₂ LB film decreases with increasing pressure, reaching a 0.6- times smaller value at 0.7 GPa. Then the pressure cell was clamped at 0.7 GPa and was cooled down to 0.5 K. A different sample strip cut from the same sample batch was also set outside the pressure cell and the ambient resistance was measured as the reference. The sample clamped at 0.7 GPa shows a distinct resistance decrease below 1.4 K on cooling, while that under ambient pressure shows a blunt decrease below 0.85 K and it turns to increase below 0.65 K. The distinct resistance drop on cooling is possibly due to a pressure-induced superconducting phase. The measurements under higher pressure and/or magnetic fields are now in progress. Reference [1] Y.F. Miura et al., Jpn. J. Appl. Phys. **37** (1998) L1481. [2] Y.F. Miura et al., Solid State Commun. **113** (2000) 603. [3] Y.F. Miura et al., Synth. Met. **120** (2001) 727. [4] G. Steimecke et al., Phosphorus Sulfur **7** (1979) 49.

GG10.41

Signatures of Quantum Transport in Self-Assembled Epitaxial Nickel Silicide Nanowires. Taehoon Kim², J. F. Lin², Zhian He³, Jon P. Bird², David J. Smith^{4,1} and Peter Bennett^{1,3}; ¹Physics, Arizona State University, Tempe, Arizona; ²Electrical Engineering, Arizona State University, Tempe, Arizona; ³Science and Engineering of Materials Program, Arizona State University, Tempe, Arizona; ⁴Center for Solid State Science, Arizona State University, Tempe, Arizona.

We have measured the electrical properties of self-assembled epitaxial NiSi₂ nanowires (NWs) formed by deposition of 1 monolayer Ni on stepped Si(111) in UHV at 500 C. This forms NWs with a single orientation and average dimensions 15 nm wide by 1.5 microns long. Samples are removed from UHV and leads are connected using electron-beam lithography with PMMA and metal lift-off. The transport measurements show quantum corrections due to weak antilocalization and electron-electron interactions. Analysis of the magneto-resistance indicates that electron phase coherence in the NWs is limited by Nyquist dephasing below 10 K, and by electron-phonon scattering at higher temperatures. The phase-breaking and spin-orbit scattering lengths are found to be 45 nm and 3 to 7 nm, at 4.2 K, respectively, similar to values for thin epitaxial NiSi₂ films.

GG10.42

Investigation of the Contact Formation Between Macro-Molecular Building Blocks and Mesoscopic Electrode Materials. Niels Dam, Brian Doran, J. Chris Braunagel, Martin M. Beerbom and Rudy Schlaf; Electrical Engineering, University of South Florida, Tampa, Florida.

The contact formation between macro-molecular building blocks (nano-particles, nanotubes, oligonucleotides, peptides etc...) and mesoscopic electrode materials (metals, semiconductors, dielectric materials) is currently not very well understood. This is for example indicated by the considerable range of recent experimental results with regard to deoxyribonucleic acid (DNA) conductive properties, which have been found to be insulating, semiconducting and metallic. It is likely that the various methods and materials used to connect to single DNA strands led to a variety of contact structures, ranging from tunneling barriers, to Schottky or Ohmic type. In this context we have developed a measurement methodology to gain detailed insight into the electronic structure of macro-molecular interfaces, and to determine the charge injection barriers. This method is based on an established technique using photoemission spectroscopy and in-vacuum preparation of the to be investigated interface. In-vacuum deposition has been traditionally an issue for large molecules due to their high mass in combination with thermal fragility, effectively preventing in-vacuum evaporation. The enabling technique used in our experiments is electrospray (ES) thin film deposition, which allowed us to prepare macro-molecular thin films in vacuum without significant contamination. Here, we present first results of this technique on ribonucleic acid (RNA)/metal interfaces, which serve as a model

system for DNA interfaces. In our experiments, we have successfully been able to deposit RNA polymers directly from solution in an UHV environment by ES. Using this method, the charge injection barriers between RNA and Au, and between RNA and highly oriented pyrolytic graphite (HOPG) were determined by depositing RNA thin films in several steps in-situ without breaking the vacuum. The deposition series started at sub-monolayer coverage on the in-situ sputter-cleaned (Au) or cleaved (HOPG) substrate surfaces. Before growth and in-between deposition steps monochromatic x-ray and ultraviolet photoemission spectra (XPS, UPS) were measured, resulting in a series of spectra allowing to follow the interface electronic structure development as the deposited layer increases in thickness. This enabled the direct determination of the orbital alignment, and the nature of the chemical interaction at the interfaces.

SESSION GG11: Structure and Intrinsic Properties of
Meso Assemblies II

Chairs: Paul Braun and Alexander Wei
Thursday Morning, December 2, 2004
Room 311 (Hynes)

8:30 AM *GG11.1

Intrinsic Properties of Nanocrystal Self Assembled.

Marie-Paule Pileni, Laboratoire LM2N, University P et M Curie, Paris, France.

Various self-organization of nanocrystals will be presented with formation of 2D compact hexagonal network, 3D supra crystals in FCC structure, ring, dots, lines, tubes and labyrinths. The collective properties induced by the self-organization are mainly due to dipolar interactions. However intrinsic collective properties are also observed. As example vibrational coherence is discovered in 3D FCC supracrystalline arrangements of silver nanocrystals. This coherence is made evident in low-frequency Raman scattering by the narrowing of the peak due to the quadrupolar modes of the nanocrystals. However, as predicted by theory, this narrowing is not visible when the sizes of the supracrystals become comparable or larger than the light wavelength. Furthermore, the supracrystallization is manifested by the shift to low frequency of the Raman peak due to the Lorentz electric field created by the light induced plasmon-polarization of the nanocrystals in the supra crystal. Another intrinsic property of supra crystal formation is crystallization process occurring at low temperature whereas it is usually observed at high temperature. This opens a new area in the crystal growth domain. Finally we demonstrate that the nanocrystals are used as mask for lithography

9:00 AM GG11.2

Ordered and Non-Ordered Heterocoagulation of Ultrafine Particle Systems. Garry R. Maskaly^{1,2}, W. Craig Carter¹ and

Yet-Ming Chiang¹; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²C-PCS, Los Alamos National Laboratory, Los Alamos, New Mexico.

The heterocoagulation of colloidal particles is a widely studied topic and the subject of an extensive body of literature. In recent work, we have found certain regimes where the suspension behavior cannot be explained by existing heterocoagulation theory. At low ionic strengths and/or small particle sizes, charge balance effects can cause a limiting heterocoagulate size such that the solution is stable for long times despite a similar number of positively and negatively charged particles. A shift in behavior from a stable suspension to a colloidal gel to a dense colloidal glass is observed as the electrostatics of the system are altered. This anomalous heterocoagulation behavior is of special interest for the formation of ionic colloidal crystals, where a dense colloidal heterocoagulated liquid is necessary to allow the nucleation and growth of complex ordered ionic structures. We present an electrostatic model that can explain this behavior. The nucleation behavior of ionic colloidal crystals from a dense colloidal liquid is also studied via Monte Carlo simulations allowing the calculation of the nucleation barrier.

9:15 AM GG11.3

Ordered Binary Structures and Self-Assembly of Shape Controlled Nanocrystals. Elena Shevchenko^{1,2}, Dmitri V.

Talopin², Stephen O'Brien¹ and Christopher Murray²; ¹Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York; ²T.J. Watson Research Center, IBM, Yorktown Heights, New York.

The monodisperse nanocrystals can self-assemble into one-, two- and three-dimensional superstructures. Various magnetic (CoPt₃, FePt, Fe₂O₃, CoPd₂) and semiconductor (CdSe, PbSe) nanocrystals were used as building blocks for the formation of 2D and 3D ordered superstructures. Systematic investigation was performed to reveal the conditions favouring formation of ordered binary superlattices. We

have investigated the effect of various stabilizing agents, solvents, temperature, size ratio and nanoparticle concentration on the formation of binary assemblies. As model systems, we used the mixtures of differently sized Fe₂O₃, CoPt₃ - Fe₂O₃, PbSe - Fe₂O₃, CdSe - Fe₂O₃ nanocrystals. For all these combinations, ordered AB₂ and AB₁₃ binary assemblies have been successfully and reproducibly formed. Perfectly faceted macroscopic (20 - 100 microns) colloidal crystals of CoPt₃, PtFe, Fe₂O₃ and CdSe nanocrystals have been grown. HRSEM investigation showed the long range ordering of the nanocrystals with the coherence over entire colloidal crystal. Colloidal CdSe nanorods and CdSe/CdS nanorod heterostructures were self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanorods can form nematic, smectic and crystalline phases with ordering in both lateral and longitudinal directions. Self-assembled CdSe nanorods can form spherulitic textures with characteristic birefringence in a light microscope. CdSe/CdS nanorod heterostructures were self-assembled into highly luminescent superlattices with low re-absorption effects.

9:30 AM *GG11.4

Binary Nanocrystal Superlattices: A Route to Multi-

functional Nanomaterials. Christopher Bruce Murray¹ and Elena Shevchenko^{2,1}; ¹IBM, T. J. Watson Research Center, Yorktown Heights, New York; ²Applied Physics, Columbia University, New York, New York.

Colloidal nanocrystals (NCs) with controlled shape, structure and surface passivation are increasingly available. The tunable electronic properties of semiconducting and magnetic NCs make them ideal building blocks for the nanoscale assembly. This talk will focus on the interesting superlattice systems that can be built with these NCs. The individual NCs form the basis for a combined structural, optical and magnetic study of the evolution material properties with size. These monodisperse NCs are then induced to self-organize during controlled evaporation to produce 2D and 3D superlattices (colloidal crystals, opals). The superlattices retain and enhance many of the desirable mesoscopic properties of individual nanocrystals and may now permit the systematic investigation of new collective phenomena. Procedures have been developed for assembly of Co, Ni, FePt, and Fe₂O₃ magnetic nanocrystals as well as for CdSe, PbSe, PbS, PbTe semiconductor quantum dots and quantum wires. Assemblies are not limited to a single repeat unit but now the formation of complex materials by controlled binary assembly is possible. Preliminary examples of superlattices with AB₁₃, AB₂ and AB₅ structures will be discussed.

SESSION GG12: Novel Responses and Applications of
Meso-assemblies I

Chairs: Albert Schenning and Humberto Terrones
Thursday Morning, December 2, 2004
Room 311 (Hynes)

10:30 AM *GG12.1

Self-Assembly and Magnetic Switching of Cobalt Nanoparticle Rings. Alexander Wei¹, Steven L. Tripp¹ and Rafal E.

Dunin-Borkowski²; ¹Chemistry, Purdue University, West Lafayette, Indiana; ²Materials Science, University of Cambridge, Cambridge, United Kingdom.

Dispersions of single-domain Co nanoparticles are capable of assembling into bracelet-like nanorings as a result of magnetic dipolar interactions. Investigations by TEM demonstrate that the self-assembled nanorings are kinetically stable, and that their mechanism of self-assembly is distinct from hole nucleation and other deposition effects mediated by solvent evaporation. Off-axis electron holography reveals that nanoparticles collectively form chiral flux closure (FC) domains when assembled into rings. Such binary states are stable at room temperature, and have intriguing potential as nonvolatile memory elements. We have recently determined that the polarity of the FC states can be switched reliably by out-of-plane magnetic fields; mechanisms for this magnetization reversal will be discussed.

11:00 AM *GG12.2

From Nanoscale Building Blocks to Macroscopic Devices.

Yunfeng Lu, Donghai Wang, Byron McCaughey, Rong Kou, Maria P. Gil and Xuan Li; Chemical & Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

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 static and responsive self-assembly. For example, we utilized self-assembled mesoporous silica as templates and electrodeposition to synthesize 2D and 3D nanowire thin films. These robust nanowire thin films show promising applications in fuel cells, thermoelectric, hydrogen separation, high surface area electrodes, magnetic materials, photovoltaics, sensors, and other applications. This presentation will also discuss the synthesis of chromatic polydiacetylene nanocomposites that show reversible dynamic transitions through responsive self-assembly approach.

11:30 AM GG12.3

Surfactant and Polymer Templated Mesoporous Metals in 2 and 3 Dimensions. Martin Gerard Bakker^{2,1}, Roger Campbell², Claude Treiner³, Jean Chevalet³ and Francois Dardoize³, ¹Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Alabama; ²Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama; ³Laboratoire Liquides Ioniques et Interfaces Charge'es, Universite' Pierre et Marie Curie, Paris, France.

Soft templating using self-assembled surfactants or block co-polymer can be used to prepare very high surface area metal surfaces for use as electrocatalysts and as porous electrodes in applications such as batteries, fuel cells, sensors and supercapacitors. Work carried out by the groups of Attard and Bartlett showed that non-ionic surfactants can be used as templates to produce thin films of metals with a regular hexagonal pore arrangement. Such thin films have surface areas which are as much as 200 fold higher than that of the planar electrodes. We have recently demonstrated that non-ionic block co-polymers consisting of poly(oxyethylene) and poly(propyleneoxide) blocks can also be used as templates from which thin metal films with a regular arrangement of pores can be electrodeposited. Using Pluronic P123 as template a hexagonal array of pores with a pore to pore spacing of 7.5 nms is produced from both nickel and cobalt salts. The conductivity of the block co-polymer solutions appears to be somewhat lower than that for the non-ionic surfactants leading to thinner films for equivalent electrodeposition times, and so somewhat smaller surface area enhancements. However, the demonstration that block co-polymers can also be used as soft templates for such systems holds the promise of a wider range of structures and length scales than is available with surfactants. We have also extended the application of such materials to three dimensional substrates, specifically nickel foam such as is used in nickel/cadmium and nickel/metal hydride batteries. For such systems we see a large surface area enhancement after formation of a mesoporous nickel film. Preliminary evidence indicates that the mesoporous film is formed throughout the nickel foam.

11:45 AM GG12.4

Synthesis and Assembly of Engineered Metal-Oxide-Metal Nanowires. Jason Tresback and Nitin P. Padture; Metallurgy and Materials Engineering, University of Connecticut, Storrs, Storrs, Connecticut.

There has been growing interest in the "bottom up" approach to building nanoelectronic devices, where nanoscale building blocks, such as nanowires (metals, semiconductors, oxides), are fabricated in isolation and assembled into nanocircuits. The "bottom up" approach offers several key advantages over the conventional "top down" microelectronics approach, including higher circuit densities and processing compatibility. Current nanoelectronics technology uses nanowires that are assembled across photo-lithographically deposited metal contact-pad electrodes to create devices. In this case, the length of the nanowire spanning the electrodes defines the active region, which is very difficult to control precisely. In order to address this critical issue, we propose the concept of the engineered metal-oxide-metal (MOM) nanowire, which is a metal nanowire (50 to 100 nm diameter; Au or Pt) with a small segment (50-100 nm length) being replaced by a functional oxide. In other words, a MOM nanowire has a functional oxide of precise dimensions with metal interconnects integrated within the building block. The functional oxide can be a sensor, ferroelectric, dielectric, semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication and control. We have used two different methods of electrochemical deposition within porous templates to synthesize such MOM nanowires. Both methods are generic, and they can be used to fabricate a wide variety of MOM nanowires. Here we have synthesized two specific examples of MOM nanowires: Au-SnO₂-Au (sensor) and Au-BaTiO₃-Au (ferroelectric). Synthesis methods, characterization results from the MOM nanowires, and the assembly of the nanowires into functional nanodevices will be presented.

SESSION GG13: Novel Responses and Applications of Meso-assemblies II

Chairs: Nicholas Kotov and Mauricio Terrones
Thursday Afternoon, December 2, 2004
Room 311 (Hynes)

1:30 PM *GG13.1

Self-Assembled P-Conjugated Systems. Albert Schenning, Eindhoven University of Technology, Eindhoven, Netherlands.

Supramolecular chemistry, which makes use of self-assembling molecular units, offers an excellent tool to construct cheaply and easily electronic components in the nanometer range. If p-conjugated oligomers are used as building blocks in these nanosized components one can expect new, unprecedented electrooptical properties. During my presentation, examples will be given on how p-conjugated systems can be self-assembled and applied in supramolecular electronics.

2:00 PM GG13.2

On-Demand Control of Optoelectronic Coupling in Gold Nanoparticle Arrays.** Fazila Seker¹, Patrick R. L. Malenfant¹, Michael Larsen², Azar Alizadeh¹, Kenneth Conway¹, Amit M. Kulkarni¹ and Gregory Goddard², ¹Nanotechnology Advanced Technology Program, GE Global Research, Niskayuna, New York; ²Biosciences, Combichemistry, and Characterization Technologies, GE Global Research, Niskayuna, New York.

The successful application of quantum dots in many device concepts requires the ability to predictably control interparticle separation. As a result, several strategies have been developed in the literature in an effort to address this challenge. Two popular examples include the use of complementary DNA strands to mediate reversible aggregation in solution, and the control of interparticle interactions in solid films through the engineering of shell thickness.[1,2] Despite the diversity of approaches available, they generally have a synthetic feature in common: The need for an iterative approach to controlled interparticle separation. Using gold nanoparticles, we demonstrate a method that affords dynamic control of interparticle interactions within a single material. Our approach relies on generating composite core/shell particles comprised of a gold core, and a shell of thermosensitive polymer poly(N-isopropylacrylamide) (pNIPA) to provide stimulus responsive control of interparticle coupling within particle arrays. Reversible changes in particle size were successfully translated into reversible changes in optical properties of a film consisting of assembled composite core/shell particles. Variable temperature UV-vis spectroscopy suggests that the thermally induced change in interparticle separation occurs coherently throughout the film. 1. J. J. Storhoff, A. A. Lazarides, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, G. C. Schatz, J. Am. Chem. Soc. 2000, 122, 4640. 2. C. B. Murray, C. R. Kagan, M. G. Bawendi, Science 1995, 270, 1335. **We thank Peter Codella and Hans Grade for assistance in characterization.

2:15 PM GG13.3

Exciton Recycling in Graded Gap Nanocrystal Structures. Thomas Franzl, Thomas A. Klar, Stefan Schietinger, Andrey L. Rogach and Jochen Feldmann; Physics Department, LMU Muenchen, Photonics and Optoelectronics Group, Munich, Germany.

Motivated by natural antenna complexes and by semiconductor heterostructure lasers, we present a cascaded energy transfer (CET) structure made of CdTe nanocrystals (NCs). Funnel like band gap profiles are realized applying layer-by-layer assembly to CdTe nanocrystals of distinct sizes. For high-energetic excitation, the CET structure with only one layer of red-emitting NCs emits 4 times more red light than a reference sample of equal absorbance consisting of seven layers of red emitting NCs. The super-efficient exciton funneling can be explained by a recycling of surface trapped excitons that are usually lost for photoluminescence [1]. The energy of the excitonic transition in CdTe nanocrystals can easily be tuned over the whole visible spectral range by changing their size. NCs can also be used as building blocks for mesoscale architectures, often called artificial solids. One example is a set of adjacent layers of differently sized CdTe NCs that shows high energy transfer rates [2]. We demonstrate that a band gap engineered funnel for excitation energy can be built using layer-by-layer (LbL) assembly of CdTe NCs. Directed energy transfer between layers of differently sized NCs forces the excitation energy into the active zone, i.e. into a single layer of the largest NCs placed in the center of the funnel. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra show two important features. First, there is negligible emission from the smaller sized NCs. The small particles apparently serve as donors and the excitation energy is efficiently transferred along the gradient towards the layer of the largest particles. Second there is a clear enhancement of the emission intensity of the largest NCs. The CET structure with a single emitting layer shows a 4 fold increased quantum efficiency compared to a reference sample containing 7 layers of the largest NCs. Hence the final exciton density in the single emitting layer of large

quantum dots is increased by a factor of 28. With these high exciton densities, NC CET structures are promising objects for optoelectronic devices such as nanocrystal-based optical amplifiers and lasers. 1. T. Franzl, T.A.Klar, S. Schietinger, A.L. Rogach, J. Feldmann, "Exciton recycling in graded gap nanocrystal structures" submitted 2. T. Franzl, D.S. Koktysh, T.A. Klar, A.L. Rogach, J. Feldmann, "Fast energy transfer in layer-by-layer assembled CdTe nanocrystal bilayers", *APL* 84, 2904 (2004)

2:30 PM *GG13.4

Dynamically Tunable Superhydrophobic Nanostructured Surfaces. Ashley Taylor, Paul Kolodner, Stanley Pau, Alan Lyons and Tom Krupenkin; Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Dynamic control over the interaction of liquids with a solid substrate is of great interest in many research areas ranging from biology and chemistry to physics and nanotechnology. Only recently, studies have been expanded to include dynamic control over the interaction of liquids with nanostructured surfaces. In this work, the properties of recently demonstrated electrically tunable nanostructured superhydrophobic surfaces are further investigated. The dependence of the superhydrophobic wetting transition on the topography of the nanostructured layer, its electrical properties, and its surface coating are investigated. The reversibility of this transition and its dependence on the geometry of the nano-size features are discussed. The reported results provide novel methods of manipulating liquids at microscale. A wide range of applications, including micro- and nanofluidics, chemical microreactors, sensors, integrated thermal management in microelectronics, and optics communications may benefit substantially from the ability to dynamically tune the liquid-solid interactions.

3:30 PM *GG13.5

Nanomaterial Properties Switched by Double-Layer Charge Injection and Retained in Vacuum. Dong-Seok Suh¹, Alan G. MacDiarmid¹, Edgar Munoz¹, W. Joshua Kennedy², Zeev V. Vardeny², Anvar A. Zakhidov¹, Vladimir Agranovitch¹, Alan B. Dalton¹, Steve Collins¹, Mei Zhang¹, Von H. Ebron¹, John P. Ferraris¹, Ali Aliev¹, S. Lee¹ and Ray H. Baughman¹; ¹Department of Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, Texas; ²Department of Physics, University of Utah, Salt Lake City, Utah.

We discovered a surprising generic method for charge-injection-based tuning of the bulk properties of electrolyte-free nanostructured materials over a wide range without incurring dopant intercalation and associated problematic structural changes. Specifically, we found that carbon nanotube sheets, nanoporous metals, and other nanostructured materials, retain injected charge and associated structure and properties changes when non-faradaically injected with charge in a liquid-electrolyte supercapacitor and then removed from the electrolyte and dried in vacuum. Charge injection for carbon nanotube sheets in an electrochemical cell causes a quasi-parabolic order-of-magnitude increase in electrical conductivity, much of which is retained when the electrolyte is either evaporated or frozen. The implications of these discoveries are explored for diverse devices that function without electrolyte contact with electrochemically switched elements.

4:00 PM GG13.6

Efficient and Reliable Fabrication of CNT Point Electron Sources by Dielectrophoresis. Jian Zhang¹, Jie Tang^{1,2}, Guang Yang¹, Qi Qiu³, Lu-Chang Qin^{1,4} and Otto Zhou^{1,4}; ¹Physics and Astronomy, UNC-CH, Chapel Hill, North Carolina; ²National Institute for Material Science, Tsukuba, Japan; ³Xintek Inc., Chapel Hill, North Carolina; ⁴Curriculum in Applied and Materials Sciences, UNC-CH, Chapel Hill, North Carolina.

Although carbon nanotubes (CNTs) have shown great promise for enabling nano-scale electronic devices, efficient and reliable methods for assembly and integration of CNT are still currently lacking. Here we report the fabrication and electron field emission properties of short CNT tips by dielectrophoresis. Aligned CNT tips comprising either SWNT bundles or MWNTs were assembled on sharp metal wires with controlled length, diameter and orientation. Over 90% of the tips were confined within 10° degree angle from the cone axis of the metal wire. Due to the interfacial morphology they adhere strongly to the metal supports, which ensure the stability under high electrical field and minimizes mechanical vibration. The CNTs are capable of delivering high and stable electron field emission currents of 3-5 μA (10^5A/cm^2 in density). The emitters thus fabricated can potentially be used as the field emission electron sources for precision vacuum electronic instruments such as electron microscopes.

References: J. Tang, et al., *Adv. Mater.*, 2003. 15(15): p. 1352. J. Zhang, et al., *Adv. Mater.*, in press

4:15 PM GG13.7

Fabrication and Characterization of Carbon Nanotube-Based AFM Probes by Dielectrophoresis. Jie Tang^{1,2}, Guang Yang², Qi Zhang², Ben Maynor³, Jie Liu³, Lu-Chang Qin² and Otto Zhou²; ¹National Institute for Materials Science, Tsukuba, Ibaraki, Japan; ²University of North Carolina, Chapel Hill, North Carolina; ³Duke University, Durham, North Carolina.

Jie Tang, University of North Carolina and National Institute for Materials Science, Tsukuba, Japan; Guang Yang, Qi Zhang, University of North Carolina, Ben Maynor, Jie Liu, Duke University, Lu-Chang Qin, Otto Zhou, University of North Carolina. Dielectrophoresis is often used to manipulate and assemble colloidal particles, and has recently been applied to carbon nanotubes (CNTs) [1]. We here present a reliable and high throughput dielectrophoresis method for fabrication of CNT-based atomic force microscope (AFM) tips at room temperature. An alternating-current (AC) electrical field was used to align and assemble the CNTs dispersed in a liquid onto the apex of a commercial AFM probe. The tip length and orientation are controlled and predetermined. They are typically 0.5 to 10 μm in length and 20 - 80 nm in diameter. Their ability to image structures with high aspect ratios will also be demonstrated. Morphological characterization using scanning electron microscope (SEM) and transmission electron microscopy (TEM) will also be presented. The dielectrophoresis method can also be extended to the fabrication of AFM and STM probes using other nanostructured materials. [1] J. Tang, B. Gao, H.Z.Geng, O.D. Velev, L.C. Qin, and O. Zhou, *Adv. Mater* 15, 1352 (2003).

4:30 PM GG13.8

Novel Approach to the 3-D Fabrication and MicroSynthesis of Functional Molecularly Imprinted Polymer (MIP) Using Microstereolithography and Microfluidic Droplet Reactors. Kyung M. Choi^{1,2,3}, John A. Rogers^{2,3} and Kenneth J. Shea¹; ¹Chemistry, University of California-Irvine, Irvine, California; ²Materials Science and Engineering, University of Illinois at UC, Urbana, Illinois; ³Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Microfabrication technology offers us rapid assembly and integration of unconventional devices since small features fabricated on a variety of substrates have produced numerous active devices, which satisfy a set of our demands in miniaturization. Especially in the development of advanced plastic/organic/molecular electronics, this technology allows us to produce economic devices with high performance using 'soft' organic/polymeric materials. Organic photoresists such as SU-8 have been widely used for pattern fabrication. Recently, there is a growing interest in the pattern integration using functional materials. In this work, we present a novel approach to the 3-D microfabrication and microsynthesis of unconventional functional materials to expand current technology to advanced levels for our diverse demands. Here, we introduced a molecularly imprinted polymer (MIP) as a promising candidate of advanced patterns with specific functions. MIP is a highly cross-linked macroporous thermoset with both high internal surface areas and specific 'molecular recognition binding sites', which may be useful for chemical or bio-sensor applications. Using the MIPs' system attached with fluorescent template molecules, we fabricated a 3-D molecular architecture in the (600 μm x 600 μm x 100 μm)-geometry through 'microstereolithography'. We also generated a fluorescent MIP pattern in 100 μm line-width by 'micromolding technique' in capillaries using PDMS microchannel photomasks. In this work, we also introduced a novel approach to synthesize nano- or micro-sized MIPs polymer particles using a 'microfluidic droplet reactors'. As the MIPs particle size was decreased, we obtained MIPs particles with higher affinity. This is a new method to produce 'monoclonal MIPs particles', which have only high affinity binding sites with specific molecular recognition function.