

SYMPOSIUM P

Self-Assembled Nanostructured Materials

April 22 – 25, 2003

Chairs

C. Jeffrey Brinker

Sandia Natl Labs/Univ. of New Mexico
Advanced Materials Laboratory
Albuquerque, NM 87106
505-272-7627

Yunfeng Lu

Chemical Engineering
Tulane Univ
New Orleans, LA 70118
504-862-8000 x5827

Markus Antonietti

Dept of Colloid Chemistry
Max Planck Inst-Colloids & Interfaces
Research Campus Golm
Potsdam, D-14424 GERMANY
49-331-567-9501

Chun-Li Bai

Inst of Chemistry
Chinese Academy of Sciences
Beijing, 100864 CHINA
86-10-68597600

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)

as Volume 775

of the Materials Research Society
Symposium Proceedings Series

* Invited paper

8:30 AM P1.1

IN-SITU X-RAY SCATTERING STUDIES OF EVAPORATION INDUCED SELF-ASSEMBLY OF MESOSTRUCTURED SILICA FILMS USING BRIJ SURFACTANT TEMPLATES. Bernd Smarsly, Dhaval Doshi, Zhu Chen, C. Jeffrey Brinker, Center for Micro-Engineered Materials, Univ of New Mexico, Albuquerque, NM; Alain Gibaud, Arnaud Baptiste, Université du Maine, Faculté des Sciences, Le Mans, FRANCE.

The formation mechanism of surfactant-templated mesostructured thin silica films was studied by in-situ grazing incidence small-angle scattering (GISAXS) at the X22B beamline at Brookhaven National Labs. Starting from an ethanol-rich solution containing nonionic Brij surfactants as the structure-directing agent and hydrolyzed tetraethylorthosilicate (TEOS) as the silica precursor, real-time 2D GISAXS pattern were obtained during the self-assembly process induced by ethanol evaporation. In addition, the GISAXS data could be exactly related to the composition of the solution by in-situ monitoring the weight loss of solvent as a function of time. This experimental setup allowed comparing the subsequent steps in the mesostructure formation in thin films with those in the bulk nanocomposite material. For the final film mesostructure, the GISAXS experiments revealed a 2D hexagonal structure that consists of cylindrical rods lying parallel to the substrate surface, confirmed by electron microscopy. The exact diameter of the cylinders was determined by detailed reflectivity experiments. Also, a well-defined intermediate 3D cubic structure was observed in the case of Brij 58 (poly(oxyethylene) cetyl ether). In order to complement the GISAXS experiments, the phase diagram of the system Brij 58/H₂O (Silica)/Ethanol (bulk material) was determined by additional SAXS (transmission) experiments. It is seen that Brij 58 predominantly forms a lyotropic phase with a primitive cubic mesostructure. This phase behavior can be attributed to the comparably long EO chains resulting in soft sphere micelles, which are known to align themselves in a bcc arrangement. Our study indicates that the mesostructure is strongly influenced by the presence of siliceous species and additional constraints of the silica network condensation, which is of general interest in the field of self-assembled silica structures.

8:45 AM P1.2

CHARACTERIZATION BY HIGH RESOLUTION 1H SOLID STATE NMR OF MESOSTRUCTURED ORGANOSILICAS. L. Camus, V. Goletto, C. Bonhomme, F. Babonneau, Chimie de la Matière Condensée, UPMC, Paris, FRANCE; R. Graf, Max-Planck-Institut fuer Polymerforschung, Mainz, GERMANY.

A large variety of periodic mesostructured organosilicas can be prepared by co-condensation of trialkoxysilane, RSi(OR)₃ and tetraalkoxysilane, Si(OR)₄ in the presence of surfactants. We have previously demonstrated that the nature of the R group can strongly influence the structure of the self-assembled materials. In the presence of phenyl groups with cetylmethylammonium bromide as surfactant, 2d-hexagonal as well as cubic Pm3n phases can be obtained. The formation of this cubic phase suggests that the phenyl groups may play an active role in the self-assembly process by specifically interacting with the polar head groups of the surfactant. In order to characterize the location of the various organic entities with respect to each other, a 1H solid state investigation has been conducted on one hexagonal and one cubic samples in high field (17.7 T) and under fast Magic Angle Spinning (MAS) (25-30 kHz). One of the most sensitive NMR experiments to probe dipolar couplings in solids, and thus spatial proximity, is the double-quantum (DQ) NMR experiment under fast MAS. First 1H-13C CP correlation experiments were performed to get a precise assignment of the 1H signals especially those of the phenyl rings (ortho meta, para positions) and of the polar head groups (N-CH₃, N-CH₂). Then, the DQ experiments on the two samples have been performed using the Back-to-Back recoupling sequence, and showed clearly the existence of coherences between the CTAB molecules and the aromatic protons. A detailed analysis of these experiments will be presented, which can lead to a precise localization of the organic entities at the interface.

9:00 AM P1.3

SPHERICAL MESOCELLULAR SILICA FOAM FOR CHROMATOGRAPHIC APPLICATIONS. Thomas M. Lancaster and Jackie Y. Ying, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Mesocellular foams are a class of high surface area and ultra-large pore volume silica supports. The silica foams exhibit large pore sizes (10-35 nm) and an interconnected mesoporous framework that facilitates the diffusion of large molecules and the hosting of sterically

demanding organometallic complexes within the structure. Thus, silica mesocellular foams (MCF) are excellent candidates for separation applications. MCF silicates are synthesized via a supramolecular templating technique. The synthesis scheme utilizes the P123 Pluronic triblock copolymer surfactant, which contains two hydrophilic blocks separated by a hydrophobic block. When added to water, the surfactant spontaneously forms micelles whose size can be tailored via the addition of 1,3,5-trimethylbenzene in solution, allowing for a high degree of control over the ultimate pore size and morphology. Tetraethoxysilane, the silica source, is then added to the mixture and condenses around the micelles at low pH to give rise to the unique MCF materials. We have manipulated MCF synthesis parameters to obtain spherical particles in the size range of 2-10 microns, while retaining the unique pore structure, large pores (25-35 nm) and narrow pore size distributions of MCF materials. In addition, the spherical MCF particles exhibit narrow particle size distributions. Further studies into the MCF synthesis have led to control over the particle size and pore size, and have allowed these parameters to be varied independently from each other. This flexibility, along with the desirable properties of MCF and a well-defined spherical particle morphology, makes these materials excellent candidates for use in separations.

9:15 AM P1.4

TAILOR-MADE NANOSTRUCTURED ION SELECTIVE MCM-48 MEMBRANES. S. Roy Chowdhury, R. Schuhl, K. Keizer, A. van den Berg, J.E. ten Elshof, MESA Research Institute, University of Twente, Enschede, THE NETHERLANDS.

MCM-type oxides with ordered mesoporosity are promising materials for emerging applications in several fields such as catalysis, sensors and separation science. In view of their high porosity and well ordered geometries with narrow pore size distributions and low tortuosities, thin films of MCM-type materials are potential candidates for membrane applications. A disadvantage of thin films with MCM-41 mesostructure for membrane applications is that the main transport paths tend to run in a direction parallel to the membrane surface. This will result in a high tortuosity in the direction perpendicular to the substrate. MCM-48 has a percolative 3D pore structure, so that a relatively low tortuosity in all directions may be expected. Applications of thin silica films with MCM-48 mesostructure as ion-selective membranes are demonstrated in the present study. MCM-48 layers deposited on conventional macroporous α -alumina supports can be used in the recovery of large molecules with high added value such as polyoxometalate (POM) catalysts. The ion retention properties and liquid permeability of solvents in MCM-48 are compared with that of a conventional mesoporous γ -alumina membrane. The second type of application concerns the development of an ion-selective interconnect between two microfluidic channels in micro-total analysis devices or micro-chemical systems. The support is a 1 micron thick silicon-based microsieve with circular-shaped perforations of 0.5-1 μ m diameter. The MCM-48 layer is deposited as a thin film covering the substrate and filling the pores, effectively resulting in a regular 2D array of micrometer-sized self-standing MCM-48 membranes.

9:30 AM P1.5

PHOTORESPONSIVE INORGANIC-ORGANIC HYBRID MATERIALS. Nanguo Liu^a, Zhu Chen^a, Darren R. Dunphy^b, and C. Jeffrey Brinker^{a,b}. ^aDepartment of Chemical and Nuclear Engineering and Center for Micro-Engineered Materials, University of New Mexico; ^bSandia National Laboratories.

In the burgeoning field of mesoporous hybrid materials, various organic ligands, including phenyl, alkyl, aminoalkyl, cyanoalkyl, thioalkyl, epoxy, and vinyl groups, have been successively incorporated onto the pore surfaces or into the frameworks of mesoporous materials. However, to date, these modifications have provided mainly "passive" functionality, such as controlled wetting properties, reduced dielectric constants, or enhanced adsorption of metal ions. By comparison, materials with "active" functionality would enable properties to be dynamically controlled by external stimuli, such as pH, temperature, or light. In an effort to make such responsive materials, we synthesized an organosilane, 4-(3-triethoxysilyl-propylureido)azobenzene (TSUA) and a bridged silsesquioxane, 4,4'-bis(3-triethoxysilylpropylureido)azobenzene (BSUA). Trans-cis isomerization induced by light or heat of azobenzene ligands contained in TSUA and BSUA cause a dimensional change in ca. 3 Å. Surfactant-directed assembly (SDA) was adopted to incorporate TSUA molecules into an ordered, periodic silica framework to make the first reported photo-responsive, self-assembled nanocomposite film. In this synergistic nanocomposite, the 3-dimensional organization of the responsive ligands allows transduction of photo energy into a useful mechanical response of interest for molecular valves or gates. The BSUA compound self-assembled via multiple intermolecular H-bonds and π - π interactions into a well-ordered supramolecular lamellar structure

exhibiting the trans- or cis- forms depending upon light exposure during self-assembly. In a dilute form, BSUA is a good precursor to make responsive hybrid nanocomposites and responsive gels in which the material properties can be controlled by external stimuli (light and heat).

9:45 AM P1.6

SINGLE-STRAND SPIDER SILK TEMPLATING FOR THE FORMATION OF HIERARCHICALLY ORDERED MESOPOROUS SILICA HOLLOW FIBERS. Limin Huang, Huanting Wang, Yushan Yan, Department of Chemical and Environmental Engineering, UC-Riverside; Cheryl Y. Hayashi, Department of Biology, UC-Riverside; Bozhi Tian and Dongyuan Zhao, Department of Chemistry, Fudan University, CHINA.

A single-strand of spider silk with diameter of ~ 5 μm and length of ~ 3 cm was used as a template to dip-coat silica-surfactant liquid crystalline mesophase along the silk direction to obtain a hierarchically ordered mesoporous silica hollow fiber (external diameter of 1-2 mm) after burning off the spider silk template and the surfactant with calcination. Spider silk can be used as a template because of its unique combination of high tensile strength, high elasticity, and high modulus. Although silk is a highly hydrophobic insoluble biopolymer, it has been shown that dragline spider silk can undergo a reversible transformation to a supercontracted state when treated in water or polar organic solvent, making it possible for any coating in hydrophilic system. Also, the surface can become totally wetted when immersed in a solution containing large amount of ethanol and surfactant. Bundles of spider silks or bacterial threads have been used as the fibrous template for coating of silica sol or magnetic nanoparticles. Until now, a single-strand of thin spider silk has not been used as a template for mesophase coating and alignment, partly because of the difficulty of collecting and manipulating single strand of spider silk. The small surface area of the thin silk is expected to produce stronger surface effect during dip-coating. Especially, when the dip-coating of silica-surfactant liquid crystalline mesophase is carried out along the silk direction, a long-range orientational ordering could be greatly favored along the silk direction due to a shear flow under gravity field. After removal of organic surfactant and spider silk by careful calcinations, a hierarchically ordered mesoporous silica hollow fiber can be finally obtained.

10:30 AM P1.7

MESOSTRUCTURED SILICA AEROGELS. N. Huesing, C. Raab, Institute of Materials Chemistry, Vienna University of Technology, Vienna, AUSTRIA.

Hydrolysis and condensation reactions of alkoxy silanes such as tetramethoxy- or tetraethoxy silanes are the "masterkey" reactions in the synthesis of porous silica-based materials. However, the sol-gel process with these precursors is limited in its potential especially when it comes to the synthesis of mesostructured monolithic materials due to the obligatory presence of the solvent as compatibilizing agent (typically an alcohol) and the catalyst to start the network forming reactions (acid or base). Diol- or polyol- modified silanes such as tetrakis(2-hydroxyethyl) silane as precursors have some distinct advantages since they can be condensed without a co-solvent, under neutral conditions (no catalyst is required to start the sol-gel reactions), and the diols/polyols released upon hydrolysis show a very good compatibility with lyotropic phases of surfactant molecules. In this work, we present the preparation of large mesostructured silica monoliths from diol-/polyol modified silanes, which exhibit a highly regular arrangement of the mesopores. The material was directly prepared from liquid-crystal like phases of block copolymer surfactants in water, followed by different drying procedures (supercritical drying, extraction of the surfactant and calcination). The influence of the synthesis condition, the drying procedure, and the removal of the surfactant on the final materials structure is discussed in detail.

10:45 AM P1.8

Abstract Withdrawn.

11:00 AM P1.9

SELF-ASSEMBLED SUPERPARAMAGNETIC MESOPOROUS MATERIALS WITH $\gamma\text{-Fe}_2\text{O}_3$ EMBEDDED IN THE WALLS. Carlos B.W. Garcia, Yuanming Zhang, Ulrich Wiesner, Cornell Univ, Dept of Materials Science and Engineering, Ithaca, NY; Francis DiSalvo, Cornell Univ, Dept of Chemistry and Chemical Biology, Ithaca, NY.

A one-pot self-assembly procedure for multifunctional nanomaterials based on nanoscopic $\gamma\text{-Fe}_2\text{O}_3$ precipitates in an aluminosilicate matrix structure directed through block copolymers is described. This provides a simple pathway to superparamagnetic mesoporous materials and nanoparticles with potential applications in magnetic separation, molecular labeling, and catalysis technologies. A combination of small and large angle x-ray scattering, transmission

and scanning transmission electron microscopy with elemental mapping as well as magnetic measurements on a SQUID magnetometer reveal a homogeneous distribution of 5-6 nm sized $\gamma\text{-Fe}_2\text{O}_3$ particles embedded in the walls of the mesoporous aluminosilicate matrix after calcination. Materials with iron loadings up to 50mol% iron on a cation basis have been synthesized without the complication of clogging the pore structure as observed in backfilled materials. The materials are stable and maintain their pore structure to temperatures as high as 800°C due to the thick walls of the matrix ($> 10\text{nm}$). The approach provides unprecedented structural control and versatility, and is expected to allow access to a variety of block copolymer based ceramic morphologies.

11:15 AM P1.10

OPTICAL AND ELECTROCHEMICAL PROPERTIES OF ORDERED MESOPOROUS TITANIA AND CERIA-TITANIA THIN FILMS WITH NANOCRYSTALLINE WALLS. Karen L. Frindell, John H. Harreld, Galen D. Stucky, Dept. of Chemistry and Biochemistry, University of California, Santa Barbara, CA.

Well-ordered cubic mesoporous titania and ceria-titania thin films have been synthesized which have walls made up of three dimensionally arranged nanocrystals with amorphous oxides at the interface. The effect of varying the ratio of cerium oxide to titania on the structural, optical, and electrochemical properties of these thin films has been investigated. It has been found that doping the titania with cerium increases the structural order and temperature stability of the mesostructure. Additionally, the addition of increasing amounts of cerium to the titania thin films exhibits significant effects on the band gap, electrochromic properties and photoresponse of the resulting mesostructured materials.

11:30 AM P1.11

MONODISPERSE MESOPOROUS MICROPARTICLES PREPARED BY EVAPORATION-INDUCED SELF ASSEMBLY WITHIN AEROSOLS. Shailendra Rathod, Timothy L. Ward, G.V. Rama Rao, Brett Andrzejewski, Gabriel P. Lopez, and C. Jeffrey Brinker, Univ of New Mexico, Dept of Chemical and Nuclear Engineering, Albuquerque, NM.

Self assembly of amphiphilic molecules or surfactants accompanied by templating of an inorganic precursor is now a well known approach to the synthesis of ordered mesoporous materials, in particular silica. This is traditionally done by spontaneous thermodynamics-driven self-assembly from a bulk solution. We have been exploring an alternative approach based on the self-assembly of amphiphilic species in solution microdroplets driven by the concentration that occurs as solvent evaporation proceeds. Using this evaporation-induced self assembly (EISA) in aerosol droplets, each droplet is a container for additives or host species present in the precursor solution. The natural internal gradients that develop in microdroplets offer further potential for development of radially-graded architectures within particles. We have been utilizing a vibrating orifice aerosol generator (VOAG) to produce monodisperse droplets of solutions containing one or more surfactants in alcohol-based or aqueous solutions of silicon alkoxide with appropriate catalysts. EISA in these microdroplets leads to monodisperse mesoporous particles in the 3-10 μm size range. Polydisperse particle populations in the micron-submicron size range have also been explored using other droplet generation methods. The choice of surfactant and alkoxide, along with solvent system and synthesis conditions, impacts the type and extent of order achieved in particles. Results from these studies will be presented. In addition, measurements of dye diffusion within particles possessing different types of mesostructure will be discussed. Accessibility of internal porosity, and control of diffusion rates are critical issues for possible applications of such particles as delivery vehicles for drugs or therapeutic agents.

11:45 AM P1.12

ULTRA THIN MESOPOROUS IRON OXIDE FILMS FROM SELF-ASSEMBLY OF MONODISPERSE NANOPARTICLES. Hong Yang and Xiaowei Teng, University of Rochester, Department of Chemical Engineering, Rochester, NY.

Template-mediated synthesis has been widely used in making ordered mesoporous and nanostructured materials in both powder and thin film forms. In this approach, surfactants and copolymers first self-assemble into ordered mesostructures in a solution phase. These structures serve as templates for inorganic and organic-inorganic precursors to form ordered mesostructured solids with different compositions and degrees of crystallinity. Although there are several different pathways and mechanisms, the formation of mesoporous powders and thin films depend on the assembled structure formed by the surfactants or copolymers. In this presentation, we report a new approach of making supported ordered mesoporous iron oxide films using a bottom-up approach. In a typical procedure, suspension of monodisperse nanoparticles of iron oxides (~ 3 to ~ 11 nm) in hexane

was allowed to self-assemble into an ordered non-close packed structure on flat solid substrates. Powder X-ray diffraction (PXRD) was used to examine the chemical compositions of the nanoparticulate precursors. The diffraction peaks at 35.5° , 43.1° and 62.5° can be assigned to $\gamma\text{-Fe}_2\text{O}_3$. The self-assembled nanoparticles coalesced locally and converted into mesoporous thin film at a moderated temperature. Quantitative microanalysis of the metal oxide wall was done by examining Fe $L_{2,3}$ edge spectra (~ 710 eV) using electron energy loss spectroscopy (EELS). The iron signals varied little when the electronic beam (lateral resolution up to ~ 2 Å) moved across the edge of hexagon, which implies the coalescence of neighboring Fe_2O_3 nanoparticles in the final film. Transmission electron microscope (TEM) analysis indicated the center-to-center distance of the final hexagonally structure could have a lateral contraction of 25% in comparison with the original honeycomb structure. For thin films generated from the assembly of 5 nm particles, this center-to-center distance is about 7-8 nm.

SESSION P2/Q4/J1: JOINT SESSION
SELF-ASSEMBLY

Chair: David J. Norris
Tuesday Afternoon, April 22, 2003
Metropolitan II (Argent)

1:30 PM *P2.1/Q4.1/J1.1

MULTICOMPOSITIONAL ASSEMBLY AND FUNCTION IN THREE DIMENSIONS. Galen D. Stucky, University of California, Dept of Chemistry & Biochemistry and Materials Dept.

Numerous examples exist, both biological and synthetic, of composite materials that are structurally organized on multiple length scales and dimensions. The 3-d organized molecular assembly of components that are both functionally and compositionally unique into an integrated system remains a challenge, albeit exciting advances in this area are being made, as evidenced by presentations in this symposium. In biogenesis the components of the system are created via non-linear parallel multivalent synthesis and processing. On the benchtop, a first approximation to this is to use a 3-d "living polymer" approach with distinctly defined chemical potential domains in which specific molecular assembly processes can be carried out on specified time scales. The overall system organization is then determined by the molecular definition of the interfaces between the domains. This talk will review some selected recent observations made on the 3-d molecular assembly of two or more inorganic species with distinct functionalities. The a priori simpler configuration of homogeneous solution-like phases makes possible electro-optic or magneto-optical composite arrays that are otherwise not easily accessible. An alternative is to carry out the molecular assembly of species with different composition and function into phase separated extended domains. An example of this is the use of block polypeptides to co-assemble capped CdSe(CdS) quantum dots and silica nanoparticles into a microcavity configuration. In this case the electronic states of the three-dimensional confined semiconductor nanocrystallites are coupled to the photonic states of the spherical microcavity to give single mode lasing.

2:00 PM *P2.2/Q4.2/J1.2

COLLOIDAL SELF-ASSEMBLY, MULTI-BEAM INTERFERENCE LITHOGRAPHY, AND PHOTONIC CRYSTALS. Pierre Wiltzius, University of Illinois, Beckman Institute for Advanced Science and Technology, Dept. of Materials Science and Engineering, Dept. of Physics, Urbana, IL.

Photonic crystals are materials that allow us to manipulate light in new and unexpected ways. Semiconducting materials played a tremendous role in microelectronics and we expect photonic crystals to revolutionize the world of microphotonics in a similar way. Colloidal self-assembly and multi-beam interference lithography are great tools to build crystals with interesting optical properties. I will review some recent progress towards constructing photonic band-gap materials and switchable 3D Bragg gratings.

2:30 PM *P2.3/Q4.3/J1.3

FORMATION OF 2D COLLOIDAL MONOLAYERS AT LIQUID SURFACES UNDER THE ACTION OF LONG-RANGE ELECTROSTATIC AND CAPILLARY INTERACTIONS. Vesselin Paunov, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM.

Recent progress on preparation of 2D structured micro-particle monolayers has demonstrated the potential application of non-specific colloid interactions between particles trapped at liquid surfaces or into liquid layers for fabrication of high technology coatings and materials. The characterization of the long-range colloidal forces operating between particles at liquid surfaces is a major step towards

understanding and controlling of the self-assembly of the particle monolayers by fine-tuning of the interparticle interactions. This presentation summarizes our findings on the long-range lateral capillary interactions between particles in several different configurations, including freely floating particles and particles trapped in a liquid film. We reveal the formal analogy between the lateral capillary interaction between particles at a liquid-fluid interface and the DLVO-type of electrostatic interaction between charged surfaces in electrolyte solution. We also analyze the super long-ranged electrostatic repulsion between charged micron-sized latex particles adsorbed at an oil-water interface. It was found that latex particle monolayers at octane-water interface remain highly ordered as a result of long-range repulsion, even on concentrated electrolyte solution. In the case of air-water interfaces, the lateral electrostatic repulsion between the particles was found to be sensitive to the electrolyte concentration in the aqueous phase. Using a laser tweezers method, we have determined the long-range repulsive force as a function of separation between two charged polystyrene micro-spheres trapped at the oil-water interface. At large separations the force is found to decay with distance to the power 4 and is insensitive to the ionic strength of the aqueous phase. The results are consistent with a model in which the repulsion arises primarily from the presence of a very small residual electric charge at the particle-oil interface. We discuss how super-structured 2D mixed monolayers of different particles can be assembled by using such long-range interactions.

3:30 PM *P2.4/Q4.4/J1.4

TOWARDS PHOTONIC INK (P-INK): A POLYCHROME COLLOIDAL CRYSTAL DEVICE. Andre C. Arsenault, Vladimir Kitaev, Geoffrey A. Ozin, and Ian Manners, University of Toronto, Chemistry Department, Toronto, CANADA; Hernan Miguez, Universidad Politecnica de Valencia, Centro Tecnológico de Ondas, Valencia, SPAIN.

We demonstrate here a planarized colloidal photonic crystal device whose optical stop-band position, width and intensity can be reversibly redox and solvent tuned over a broad wavelength range by an anisotropic expansion of the photonic lattice. The material is composed of silica microspheres in a matrix of crosslinked polyferrocenylsilane, a metallopolymer network with a continuously variable state of oxidation. Optical data was fitted using scalar wave theory, with a congruence to experimental data, allowing facile extraction of information concerning polymer swelling behaviour. The chemo-mechanical polychrome optical response of the material was exceptionally fast, attaining its fully swollen state from the dry shrunken state on a sub-second time-scale.

4:00 PM *P2.5/Q4.5/J1.5

COLLOIDAL CRYSTAL TEMPLATING OF POROUS SOLIDS FOR APPLICATIONS BEYOND PHOTONICS. Andreas Stein, Hongwei Yan, Sergey Sokolov, Justin C. Lytle, Mohammed Al-Daous, University of Minnesota, Department of Chemistry, Minneapolis, MN.

A variety of colloidal crystal templating methods have been developed to produce three-dimensionally ordered macroporous (3DOM) or "inverse opal" structures. Many studies have focussed on photonic crystals as target materials, with interesting projected applications involving confinement and control of electromagnetic waves. Structural requirements on such photonic crystals are rigorous, and strict control of defects is necessary to obtain photonic bandgaps. A number of other applications of 3DOM materials pose less rigorous requirements on structural periodicity, but benefit from the 3D arrays of relatively large interconnected pores, highly accessible surfaces, and compositional flexibility of the synthesis. Such applications include optical sensing, catalysis, battery materials, and bioactive materials. This presentation will provide a general overview of relevant issues of structural control in these applications and will then focus on 3DOM materials for nanostructured electrodes (V_2O_5 , LiNiO_2 , LiCoO_2 , LiMn_2O_4 , and SnO_2) and bioactive glasses (SiO_2/CaO).

4:30 PM *P2.6/Q4.6/J1.6

SELF-ASSEMBLY OF NANOSTRUCTURED LIQUID CRYSTALS. Takashi Kato, The Univ of Tokyo, Dept of Chemistry and Biotechnology, School of Engineering, Tokyo, JAPAN.

Self-assembly of liquid crystalline (LC) materials with functional moieties is one of versatile approaches to obtain functional molecular soft materials. Here we show two of our approaches to the fabrication of functional LC materials built by non-covalent interactions such as hydrogen bonding and ion-dipolar interactions. The combination of self-assembly through such non-covalent interactions and nanophase segregation behavior is the key for the formation of these functional structures. (1) Low-Dimensional Ion-Conductors: Phase-segregated nanostructures formed by self-assembly processes are useful for the design of functional materials such as ion and electron conductors. Macroscopically oriented one- and two-dimensional ion-conductive materials have been obtained by self-assembly of ionic liquids and

hydroxyl-functionalized aromatic molecules. They are partially incompatible and their mixtures form columnar and smectic phases. For one-dimensional conductors, macroscopic homogeneous orientation of the columnar structures is easily achieved by shearing the materials for those assembled materials at room temperature, which leads to high anisotropic ion-conductivity. (2) Ion-Induced Chiral Supramolecular Assemblies: We have designed LC folic acid derivatives having oligo(amino acid) moieties. These materials exhibit columnar and cubic phases due to the formation of hydrogen-bonded tetramers. The addition of a sodium salt induces and stabilizes the cubic phases. Moreover, the addition of the salt has induced the formation of supramolecular chiral LC assemblies. This materials design might lead to the fabrication of materials that are responsive to stimuli such as ions and environments.

SESSION P3: POSTER SESSION
SELF-ASSEMBLED MESOSTRUCTURED
MATERIALS

Tuesday Evening, April 22, 2003
8:00 PM
Golden Gate (Marriott)

P3.1
SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS OF ORGANIC-INORGANIC HYBRID MESOPOROUS SILICA PREPARED BY MICROWAVE HEATING. Jinseong Chung, Whaseung Ahn, Wonjo Cheong, Inha Univ, School of Chemical Engineering, Inchoen, KOREA.

Organic-inorganic hybrid mesoporous materials in which ethane(-CH₂CH₂-) group is homogeneously distributed in silica framework were prepared using BTME (1,2 bis(trimethoxysilyl) ethane) as a precursor and alkyltrimethylammonium chloride/bromide surfactant as a template. Depending on the synthesis conditions, either hexagonal or cubic structured material was obtained. Hydrothermal preparation of the material using microwave heating produced a hybrid material with spherical morphology with narrow particle size distribution in substantially reduced synthesis time. ²⁹Si and ¹³C-MAS NMR analysis were carried out to establish the uniform incorporation of organic fragments into the pore walls of the product. Mesopore structure with narrow pore size distribution was confirmed by TEM and N₂ adsorption isotherm. Pore size enlargement using 2,4,6 trimethylbenzene as a swelling agent also produced a highly ordered mesopore structure with minimum structural deterioration. Hydrophobic nature of the hybrid material was evaluated using organic/water adsorption capacity measurements. Morphology of the hybrid materials was examined by SEM and subsequently tested as a HPLC column material after C18 surface functionalization with/without capping treatment, demonstrating promising results for a reverse phase application. Titanium grafting or Mn-salen complex tethering on the hybrid material produced catalysts with enhanced selectivity in cyclohexene oxidation using either H₂O₂(epoxidation) or TBHP (etherification) as oxidant, due to hydrophobic nature of the support material. In addition, hybrid materials containing different proportions of BTME to TMOS or 3- mercaptopropyl trimethoxysilane were also prepared for applications as a host material for enzyme immobilization or as a solid acid.

P3.2
LUMINESCENCE PROPERTIES OF EUROPIUM-DOPED YTTRIUM OXIDES DERIVED FROM THEIR MESOPOROUS AND NANOTUBULAR DODECYLSULFATE-TEMPLATED FORMS. Tsuyoshi Kijima, Kenichi Iwanaga, Akemi Hamasuna, Shinji Mohri, Mitsunori Yada^a, Masanori Sekita^b, Masato Machida, Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, Miyazaki, JAPAN. ^aDepartment of Chemistry & Applied Chemistry, Faculty of Science & Engineering, Saga University; ^bResearch Institute for Substance and Materials.

Yttrium oxide doped with trivalent europium ions is greatly important as one of the red emitting phosphors for optical applications such as fluorescent lamps and field emission displays because of its stability towards high energy radiations. The brightness of such phosphors is strongly affected by their structural or compositional properties such as dopant concentration, crystallinity, and particle size. Previously, the authors synthesized a series of mesoporous and nanotubular rare-earth oxides templated by dodecylsulfate assemblies. This paper reports the synthesis of 1-5 mol% europium-doped yttrium oxides by calcinations of their precursors mesoporous and nanotubular materials with dodecylsulfate anions and the luminescence properties of the precursors calcined oxides. The europium doped hexagonal-structured and nanotubular yttrium oxides templated by dodecylsulfate assemblies were synthesized by the homogenous precipitation method using urea and then calcined at 1000°C. The luminescence spectra of both the precursors mesoporous and nanotubular solids at room

temperature showed a medium peak attributable to the attributable to the ³D₀ to ⁷F₂ transition accompanied by the ⁵D₀ to ⁷F₁ transition concerned with magnetic dipolar interaction. As a result of calcination only the ⁵D₀ to ⁷F₂ transitions for both systems were markedly enhanced relative to that for a bulk sample precipitated without surfactant species and then calcined under the same condition. X-ray observations suggested that the arrangement of framework atoms is amorphous or completely disordered in the precursors mesoporous solid, but less disordered in the nanotubular structure, and the bulk sample with no mesostructural character is poorly crystalline but much less disordered compared with the other two materials. The positional randomness of doped europium ions in these three systems would be reduced in this order and inherited into their calcined oxides. Thus, the marked increase of luminescence intensity for the mesostructure-originated systems may be attributed to a significant decrease of the energy dissipated during the energy transfer from active site to site.

P3.3
VAPOR TREATMENTS OF SPIN-ON MESOSTRUCTURED SILICA FILMS FOR THE ENHANCEMENT OF STRUCTURAL STABILITY. Shunsuke Tanaka, Norikazu Nishiyama, Yasuyuki Egashira, Korekazu Ueyama, Osaka Univ, Div of Chemical Engineering, Osaka, JAPAN; Yoshiaki Oku, MIRAI-ASET, Ibaraki, JAPAN.

Thin films of mesostructured materials have an ideal morphology for the possible applications in fields such as separation, sensors, low-k films, and other optoelectronic devices. A simple way to synthesize mesostructured silica films have been developed by a spin-coating. However, the structural stability of mesostructured silica films prepared by spin-coating is generally lower than the ones obtained by hydrothermal synthesis. In this study, we have developed a vapor infiltration (VI) treatment for mesostructured silica films to improve the structural stability and chemically modify the pore wall. Vapor treatments are performed with silica source, e.g., tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), trimethylchlorosilane (TMCS), and so on. X-ray diffraction (XRD) analysis suggested that the VI-treated mesostructured silica film did not contract during calcination, showing high thermal stability. Fourier transform infrared (FTIR) spectroscopy studies confirmed that the VI-treated mesostructured silica film is more hydrophobic than the untreated ones because of low concentration of the silanol groups. Thermal treatment without TEOS vapor was not effective to enhance the structural stability of mesostructured films. The quantitative analysis of the VI treatment were performed using the measurements of nitrogen adsorption/desorption, the pore wall density, and weight change under the VI treatment. These studies demonstrated that silica source molecules penetrated into originally-deposited silicate and could not deposit on the outer surface and inside the pores. The densified pore wall by successive penetration of silica source molecules has high structural stability. The VI treatment technique provides a good support for preparation of mesoporous materials. The VI-treated mesoporous silica films are promising materials such as low-k films and other optoelectronic devices.

P3.4
THERMAL AND PHOTO DECOMPOSITION OF SELF-ASSEMBLED MONOLAYERS (SAMs). Jung W. Lee, Hee K. Kim, Hyung M. Sung-Suh, Chan R. Park, Hyon T. Kwak, and Myung M. Sung.

The thermal and photo decomposition of octadecyltrichlorosilane(OTS)- and perfluorodecyltrichlorosilane(FTS)-based self-assembled monolayers(SAMs) in air have been studied using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and contact angle analysis. It is found that the FTS monolayers are stable in air up to about 400°C while the OTS monolayers decompose in air above 220°C. Both the monolayers primarily decompose through C-C bond cleavage, with a gradual reduction in chain length. Photodegradation studies on FTS monolayers reveal a quite different mechanism as the OTS monolayers, i.e., decomposition through C-C bond cleavage.

P3.5
SOL-GEL SYNTHESIS OF INORGANIC-ORGANIC SILICA-BASED MATERIALS CONTAINING PHARMACEUTICAL MOLECULES. Ansgar Bögershausen and Hubert Koller, Institute of Physical Chemistry, University of Münster, GERMANY.

Pharmaceutical molecules (e.g. Persantin) are immobilized into silica-based hybrid materials during the hydrolytic polycondensation (sol-gel chemistry) using tetraethylorthosilicate (TEOS = Q group) and a second precursor, R-Si(OEt)₃ (= T group). Several parameters have to be controlled in the sol-gel synthesis (e.g. pH of the hydrolysis and condensation process, hydrolysis time, concentration of the

monomer precursors). The dried xerogels are characterized with ^{29}Si solid state NMR spectroscopy to get information about the degree of condensation. ^{13}C CP MAS NMR and IR experiments show that the drug molecule is intact after the synthesis. The influence of the synthesis route on the release of the drug is observed in dissolution rate tests carried out at 37°C in 0.1% HCl. Depending on the organic group, R, up to 90% of drug are released within 17 hours. If the pH of the condensation process is varied, then the drug release profile changes. The N_2 adsorption experiments of the gels with methyl, propyl and phenyl R groups before and after the dissolution rate tests show an increase in the specific surface area, and there is a correlation between the amount of released Persantin and the specific BET surface area.

P3.6
ATOMIC LAYER DEPOSITION OF TiO_2 THIN FILMS ON SELF-ASSEMBLED MONOLAYERS (SAMs). Young J. Jang, Won J. Yoon, Jae P. Lee, Hyung M. Sung-Suh, Chan R. Park, Hyon T. Kwak, and Myung M. Sung.

The TiO_2 thin films were grown on self-assembled monolayers (SAMs)-coated Si substrates by atomic layer deposition (ALD). The structure, chemical composition, morphology, thickness of the deposited films were investigated by ultraviolet(UV) spectrometry, atomic force microscopy (AFM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and secondary electron microscopy (SEM). The results show that the growth behavior of the TiO_2 thin films is affected by chemical properties of substrate surfaces as well as the ALD conditions. In this presentation, the bottom-up fabrication techniques based on SAMs and ALD will be discussed which might be applied to the fabrication of microelectronic and other complex molecular-scale devices.

P3.7
A NEW STRATEGY FOR SYNTHESIZING ZEOLITES. Hyunjoon Lee and Mark E. Davis, Chemical Engineering, California Institute of Technology, Pasadena, CA; Stacey I. Zones, ChevronTexaco Energy and Research Center, Richmond, CA.

Syntheses of large pore zeolites and molecular sieves require the use of water-soluble organic molecules that act as structure-direction agents (SDAs) during the self assembly of these complex, hybrid, organic-inorganic composite materials. Since the SDAs are enclathrated during the synthesis, they must be removed by destruction (normally via combustion) in order to create the pore space. When preparing high void volume materials, the organic content is sufficient to produce large exotherms during the removal process that can be detrimental to the crystals. Additionally, the major costs of the assembly process is the organic SDA. In order to avoid these difficulties, we have developed a new strategy for synthesizing zeolites that involves the use of recyclable SDAs. The key concept to this strategy is to synthesize SDAs that can be easily cleaved into specified fragments AFTER the zeolite is synthesized; the cleaved fragments are extracted from the intrazeolitic void spaces because of their smaller size. The fragments can be recombined into the SDA molecules and used to synthesize zeolites again. This strategy avoids the loss of the organic component and eliminates any exposure to harsh SDA removal conditions. In order to demonstrate the feasibility of this approach, an acetal containing molecule, dimethylated ammonium derivative of 4-dioxo-8-azaspiro[4,5]decane (SDA-1), was synthesized and used as a SDA. SDA-1 was used to synthesize zeolite MFI. SDA-1 that was residing inside pores of MFI was cleaved by the reaction with H_2O -saturated hydrogen chloride gas. The cleavage of SDA-1 into the desired ketone fragment was demonstrated by using ^{13}C CP MAS NMR, IR and TGA. The intrazeolitic fragments (ketone and ethylene glycol) were removed by ion-exchange, and the remaining MFI zeolite had microporosity as measured by N_2 adsorption.

P3.8
SYNTHESIS OF MESOPOROUS METAL/ SiO_2 NANOPARTICLES AND THEIR CATALYST APPLICATIONS. J. Eric Hampsey, Qingyuan Hu, Sarah Arsenaault, Donghai Wang, Byron McCaughey, and Yunfeng Lu, Tulane University, New Orleans, LA.

Spherical mesoporous silica particles with entrapped metal nanoparticles have been synthesized using an aerosol process. The particles were produced from silica sols made from an alkoxysilane, ethanol, surfactant, water, HCl, and the metal precursors (e.g., salts or complexes). Using nitrogen as a carrier gas, the sol was sent through an atomizer producing aerosol droplets, which were passed through a tubular furnace heated to 400°C . Solvent evaporation from the droplets enriches the non-volatile components and results in co-assembly of silicate and surfactant into 3-dimensional mesostructures. Subsequent calcination of the surfactant and the metal reducing reactions result in mesoporous silica particle supported catalysts. These catalysts show high catalytic activity in

liquid and gas phase reactions. Nitrogen adsorption, transmission electron microscopy (TEM) and other techniques have been used to characterize these catalytic particles.

P3.9
SILICA HYBRID GELS WITH MOLECULAR VALVES FOR CONTROLLED DRUG RELEASE. Ansgar Bögershausen^a, Steven J. Pas^a, Pavla Meakin^b, Anita J. Hill^b, and Hubert Koller^a. ^aInstitute of Physical Chemistry, University of Münster; ^bCSIRO Manufacturing and Infrastructure Technology, Victoria, AUSTRALIA.

The anti-hypertensive drug, Persantin, is incorporated into the pores of silica hybrid gels which are synthesized from tetraethylorthosilicate (TEOS), and a second, molecular precursor, R-Si(OEt)₃. The gels have been subjected to a kinetic dissolution experiment in aqueous HCl, under controlled conditions. The release kinetics as well as the total amount of drug released, depend on the hybrid gel composition and its synthesis parameters (e.g. pH vs. time profile). The porosities of the gels before and after the drug dissolution test have been investigated with nitrogen adsorption experiments. The hybrid gels with methyl, propyl and phenyl R groups all show an increase in the specific surface area after the dissolution experiment in 0.1% HCl. Surprisingly, the materials with acetoxypropyl side chains have virtually no increase in the surface area, although these gels release the highest amount of drug. It can be concluded from SEM microprobe experiments that the drug is not precipitated on the outer surface of the particles. Other possible reasons for this surprising observation are (a) a collapse of the gel upon drug release, and (b) pore blocking at 77 K (where the N_2 adsorption is carried out). Therefore, we have performed positron annihilation lifetime spectroscopy, since positrons can penetrate matter without the need of pore accessibility to the external surface. This method clearly shows that free void space is produced in the acetoxypropyl-modified hybrid gel upon Persantin dissolution. Accordingly, the pores may have acetoxypropyl side chains blocking the produced void space at 77 K to the external surface, probably by the formation of stable hydrogen bonds. On the other hand, the side chains become sufficiently flexible at 310 K, where the dissolution of the drug is carried out, to allow Persantin to leave the interior pores. In this sense, the acetoxypropyl side groups can be viewed to function as a "molecular valve", influencing pore accessibility via temperature dependent motional properties.

P3.10
Abstract Withdrawn.

P3.11
Abstract Withdrawn.

P3.12
ORDERED MESOPOROUS SILICA FILMS SYNTHESIZED FROM VAPOR PHASE. Norikazu Nishiyama, Shunsuke Tanaka, Yasuyuki Egashira, Korekazu Ueyama, Osaka Univ, Div of Chemical Engineering, Osaka, JAPAN; Yoshiaki Oku, MIRAI-ASET, Ibaraki, JAPAN.

MCM-41 type mesoporous silica materials and mesoporous silica films have conventionally been fabricated by deposition of surfactant-silicate composites from a liquid phase under acidic or basic conditions. Here, we report a novel synthesis route of thin films made of periodic mesoporous silica, which is prepared from vapor phase. First, surfactant films were deposited on a silicon substrate by a spin coating. Then, the surfactant films were contacted with vapors, such as tetraethoxysilane (TEOS), tetramethoxysilane (TMOS), methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES). Nano-phase transition of organic-inorganic nanocomposite under vapor infiltration of silica source was found. The self-assembling (nano-phase transition) of surfactant-silicate composites under vapor infiltration implies their high mobility in the absence of solvent. The rearrangement into a hexagonal periodic structure implies high mobility of the surfactant-silicate composites in solid phase. The swelling of film thickness and d-spacing was observed under vapor infiltration. The nano-phase transition under vapor infiltration contains competitive two process: (1) the penetration of silica source into the film and (2) the reaction of the silanol groups. Film thickness and d-spacing were controlled by changing synthetic temperature, silica source, catalysts (HCl or NH_3), and the thickness of surfactant films. The films prepared from vapor-phase show superior characteristics, such as high structural stability and high resistance to water adsorption. The vapor infiltration method is a simpler process than conventional sol-gel techniques and attractive for mass production of a variety of organic-inorganic composite materials and inorganic porous materials. This novel synthetic method provides opportunities for the creation of new materials technologies.

P3.13
TEMPLATE SYNTHESIS OF NEW CUBIC MESOSTRUCTURED

SILICA FROM SERIAL REPLICATIONS OF A MCM-48 SILICA HOST. Jeong Yeon Kim, Suk Bon Yoon, Jong-Sung Yu, Department of Chemistry, Hannam University, Taejeon, KOREA.

Recently, remarkable progress has been made in the synthesis of carbons with periodic ordered structures in the range of micropores (<2 nm), mesopores (2 ~50 nm), and macropores (>50 nm) using inorganic templates such as zeolites, mesoporous molecular sieves and silica gels. In particular, a new class of mesoporous carbon materials that has attracted great interest has been reported using both cubic and hexagonal silica mesostructures as templates. In these works, a carbon precursor was incorporated into the mesopores of a silica framework to generate a mesoporous carbon templated by the sacrificial silica. In this work, we report for the first time a novel synthesis of new nanostructured silica with an ordered arrangement of uniform mesopores by nanocasting of a highly ordered mesoporous carbon template, which had itself been prepared from a mesoporous MCM-48 silica hosts. Particularly, this method using MCM-48 as a starting template offers the possibility of producing new silica materials with periodic nanostructured order not attainable through a conventional surfactant assembly process.

P3.14
SYNTHESES OF HIGHLY ORDERED MESOPOROUS AND LAYERED TITANIA WITH NEW SYNTHETIC ROUTE. Taek Young Kim, Sang Kyung Lee, Seung Yong Chae, Wan In Lee, Department of Chemistry, Inha University, Incheon, KOREA.

We report ionic surfactant-mediated syntheses of highly ordered mesoporous and lamellar titania structures by controlling the bulkiness of Ti precursors. The Ti-precursors, which are stable in basic aqueous solution, have been designed and chosen for this purpose. Mesoporous titania has a hexagonal array of mesopores with 3.0 nm, and the wall thickness is 1.5 nm. The pore structures are more highly ordered than those prepared with neutral surfactants. In the lamellar structure the interval between each titania layer is 2.8 nm, and the thickness of titania layer is 1.6 nm. The layered titania crystallographically in anatase phase is negatively charged, and positive surfactant ions are intercalated. This new layered titania has a potential application as a host material for intercalation chemistry.

P3.15
SPONTANEOUS SELF ASSEMBLY OF MCM-41 DIRECTLY INSIDE MONODISPersed SILICA SPHERES FOR CHROMATOGRAPHIC APPLICATIONS. Anne Galarnreau, Thierry Martin, Francesco Di Renzo and Francois Fajula, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, FRANCE.

MCM-41 [1] mesoporous materials have rapidly attracted many scientific communities for different potential applications like catalysis, adsorption or chromatography. For high performance HPLC, monodispersed silica spheres of 5 mm diameter are suitable. Many studies have worked on morphology control of this kind of materials by adjusting nucleation and growing steps among the self assembly of surfactants and silica alkoxydes [2-4]. But a main problem, not-overcome to date, is aggregation between particles which contributes to enlarge the width of chromatographic peaks. Our new pathway [5] allows to achieve monodispersed silica spheres without aggregation, by using spherical silica particles as starting nanoreactors. Under proper conditions, the self assembly of surfactants and silicates occurs only inside the silica particles by transforming the initial intergranular porosity into mesostructured porosity. The mechanism implies in-situ local silica dissolution and reprecipitation in presence of surfactants. A disordered materials is first formed, built from MCM-41 patches of different wall thicknesses due to the slow diffusion rate of the surfactant inside the porosity of the silica sphere. Then the amount of incorporated surfactant increases and unreacted silicates are expelled from the particles. The materials rearrange with time to yield to uniform very well ordered MCM-41 particles. This new pseudomorphic synthesis enables to vary independently the textural properties of MCM-41 without affecting the particles morphology and size, in the range 5 to 100 nm, which is hardly the case for the previous syntheses by growth control. The unique particle size distribution of MCM-41 has not only been assessed by SEM and laser granulometry, but also by chromatography which constitutes an imperative macroscopic granulometry characterization. 1. Beck, J.S. et al. 1991, Mobil: WO Patent 91/11390. 2. Boissiere, C. et al., Chem. Comm., 1999, 2047. 3. Grün, M. et al., Adv. Mater., 1997, 9, 254. 4. Yang, H. et al., J. Mater. Chem., 1998, 8, 743. 5. Martin, T. et al, Angew. Chem., Int. Ed., 2002, 41, 2590.

P3.16
Abstract Withdrawn.

P3.17
A NOVEL ETHYLENE GLYCOL BASED SILICA PRECURSOR IN

THE SYNTHESIS OF MESOSTRUCTURED SILICA MONOLITHS. Christina Raab, Viktoria Torma, Nicola Hüsing, Institute of Materials Chemistry, Vienna University of Technology, Vienna, AUSTRIA.

Lytropic liquid crystalline phases of surfactants in water are commonly utilized as structure directing agents for mesostructured materials. The conventional inorganic precursors for Si-based materials, tetraethoxysilane and tetramethoxysilane, are insoluble in surfactant/water phases without addition of co-solvents such as alcohol. Furthermore, the alcohol formed during hydrolysis is often detrimental for the supramolecular aggregates of surfactants. Tetrakis(2-hydroxyethyl)orthosilicate, an ethylene glycol ester of orthosilicic acid, is water soluble and the ethylene glycol released during hydrolysis affects the liquid crystal phases only to a minor extent which was verified by means of ²H NMR studies and POM. Non-ionic polyethylene glycol containing amphiphilic molecules such as Brij56 and the block copolymer Pluronic P123 were employed as structure-directing templates in various concentrations with tetrakis(2-hydroxyethyl)orthosilicate for supercritically dried mesoporous silica monoliths. The surfactant-templated monolithic aerogels were structurally (SAXS, TEM, ²⁹Si and ¹³C MAS NMR, N₂-sorption measurements) and chemically (elemental and thermal analysis) investigated. For certain concentrations of Brij56 and P123 the final aerogel structures show Bragg reflections in SAXS measurements indicative of a regular arrangement of mesopores which could also be confirmed by TEM. Wormlike structures and a periodic hexagonal build-up of the network were observed.

P3.18
FLUORINATED SURFACTANT TEMPLATING OF ORDERED NANOPOROUS SILICA. Stephen E. Rankin, Bing Tan, Barbara L. Knutson, Chemical and Materials Engineering Department, University of Kentucky, Lexington, KY; Hans-Joachim Lehmler, Graduate Center for Toxicology, University of Kentucky, Lexington, KY.

For several years, researchers have made controlled-porosity ceramics by sol-gel polycondensation of organosilicon precursors in the presence of supramolecular templates. Many categories of surfactants and block copolymers (cationic, anionic, and nonionic) have been used, and the structure and ordering in the product has been shown to depend explicitly on the structure of the surfactant [J.Y. Ying et al. *Angew. Chem. Int. Ed.* 1999 38:56]. We will discuss the use of a new class of supramolecular templates, fluorinated surfactants. These surfactants are considerably more surface-active, assemble more easily into ordered structures, and tend to form micellar aggregates with less curvature than ordinary hydrocarbon surfactants. We will describe a room temperature, one-pot synthesis of ordered porous silica using perfluoroalkyl pyridinium surfactants. Nitrogen adsorption, x-ray diffraction and TEM results will be presented that show that at room temperature, we have prepared particles with well-ordered 2D hexagonal pores using a surfactant with an octyl (C8) tail. The pore size determined by the inflection in the nitrogen adsorption isotherm is on the order of 2.4 nm. This interpretation is consistent both with a modified version of the Kelvin equation for nitrogen adsorption in silica mesopores, and with nonlocal density functional theory calculations. We will discuss the sensitivity of the properties of the materials to counterions, cosolvents, and the length of the perfluoroalkyl tail.

P3.19
CHARACTERIZATION OF ALUMINOSILICATE PRECURSORS OF ZEOLITES BY IN-SITU AND EX-SITU AFM OBSERVATION. Toru Wakihara, Akira Sugiyama, Tatsuya Okubo, Department of Chemical System Engineering, The University of Tokyo, Tokyo, JAPAN.

Zeolites are hydrated, crystalline tectoaluminosilicate that are constructed from negatively charged TO4 tetrahedra (T = tetrahedral atom, e.g. Si or Al). On the contrary to the formations of typical metal oxides, it is difficult to consider the zeolite crystallizations from a point of view of chemical or phase equilibria because zeolites are obtained as metastable phases and are, therefore, affected by various factors (e.g. starting composition, pH, temperature, mixing procedure, agitation and synthesis time). Accordingly, the crystallization mechanisms of zeolites have not been well understood yet. Especially, the crystallization mechanisms of low Si/Al ratio zeolites synthesized without SDAs are more complicated, because the interaction among water, alkali cations and aluminosilicate species are strong and interrelated. In this contribution, crystal growth behaviors of seeded zeolite A and faujasite were studied by ex-situ and in-situ AFM observation. In the ex-situ observation, the changes in the atomic-scale height at the same position are investigated along with the synthesis time, and it is shown that the crystal growth behaviors are different for two zeolites in the same solution. In addition, the changes in the seeded zeolite A in alkaline solution were investigated by in-situ AFM, and it was found that crystal growth and dissolution proceeded simultaneously on the same surface. By the detailed

analysis of sectional data, one of the precursors for zeolite A growth is determined as four-membered rings.

P3.20

HYPERPOLARISED ^{129}Xe NMR FOR PROBING POROSITY OF MESOPOROUS SILICA, ALUMINOSILICA AND SUPPORTED MESOPOROUS SILICA THIN FILMS. Andrei Nossov, David Grosso, Elias Haddad, Flavien Guenneau, Florence Babonneau, Clement Sanchez, Antoine Gedeon, Universite Pierre et Marie Curie, Lab. SIEN, Paris, FRANCE.

The field of mesoporous materials has experienced a burst in the last decade following the introduction of the supramolecular template approach by Beck and co-workers. The evaporation-induced self-assembly process represents an interesting way to design mesostructured organic-inorganic hybrids, which are precursors for mesoporous solids. By this process, silica and non silicate based mesoporous materials have been prepared as powder and as thin films. The main problem of these mesoporous materials and especially the thin films is related to the characterisation of their porous structure (pore size; pore volume). In the past twenty years, ^{129}Xe NMR has become a popular technique for the characterisation of porous solids. However, application of thermally polarised ^{129}Xe NMR to materials is often hampered by a relatively weak signal due to low concentration of adsorbed Xenon and long relaxation times (this is particularly the case for mesoporous silica). An increase in sensitivity of several orders of magnitude ($\times 10^4$) can be achieved by using optical pumping techniques for the production of hyperpolarised (HP) Xenon, which have made it very attractive for materials applications and should allow to probe very small quantities of matter. In the present communication we report for the first time the direct probing of thin supported films of mesoporous silica as well as results on mesoporous silica and aluminosilicate powder samples. Results on functionalized silica by organic compounds are also shown. This first application of continuous flow hyperpolarised (HP) ^{129}Xe NMR to porous films is of paramount importance because it opens a land of opportunities for the in situ characterisation of porous materials deposited as thin films on any given device.

P3.21

ORGANIC-INORGANIC INDUCED ASSEMBLIES PRECURSORS FOR COLLOIDAL PARTICLES OF CONTROLLED SIZE AND SHAPE. Corine Gerardin, Frederic Bouyer, Nicolas Sanson, Francesco Di Renzo, Francois Fajula, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, FRANCE.

Double hydrophilic block copolymers were used to control the growth and the morphology of inorganic particles and directly prepare sterically stabilized colloidal suspensions of metal hydroxide oxides. Metal hydroxides were obtained by forced hydrolysis of metal ions in the presence of the copolymers. The block copolymers contain a metal-complexing polyelectrolyte block and a neutral stabilizing block. The role of the first block, which is anionic, is to ensure a controlled growth of the inorganic phase as the complexing functions act as poisons of the inorganic polycondensation reactions; the second block, which is neutral, ensures the steric stabilization of the colloids. First, hybrid organic-inorganic aggregates form by induced assembly of the copolymers in the presence of cationic inorganic species. The assembly process is induced by complexation of the inorganic ions by the anionic blocks. The aggregates are the hybrid analogues of the well-known PolyIon Complex Micelles. Sodium polyacrylate-*b*-polyhydroxyethylacrylate copolymers were mixed with aluminum, copper or lanthanum salts, a spontaneous formation of well-defined aggregates with a finite size is observed. Dynamic light scattering and small angle neutron scattering (SANS) were used to characterize the sizes and the form factors of the aggregates. A detailed characterization of the core-corona micellar architectures was obtained by SANS. Then, the micelles have been used as adjustable supramolecular precursors for the formation of suspensions of metal hydroxides ($\text{M}=\text{Al}, \text{Cu}, \text{La}$). Total hydrolysis of the metal ions in the micellar core leads to mineralization of the colloids and formation of sterically stabilized particles with a dense inorganic core. The main parameters controlling the final particle size were identified: the copolymer-to-metal ratio, the metal prehydrolysis ratio and the polymer block lengths. Finally, the morphologies of the hairy particles depend on the nature of the metal and on some specific synthesis parameters.

P3.22

SPRAY DRYING FUNCTIONALIZED MESOSTRUCTURED COLLOIDS. Nina Andersson, Peter Alberius, Lennart Bergstrom, Institute for Surface Chemistry, Stockholm, SWEDEN.

An industrially viable production method is a prerequisite for the commercialization of mesostructured materials. Inspired by Brinker et al, who reported an aerosol-based method in 1999, we have developed a small pilot plant for the continuous production of well ordered

mesostructured materials ($>10\text{g/h}$) which can easily be scaled to an industrial process. The method is based on a modified spray drying equipment. It combines advantages of thin film preparations, e.g. control over internal structure, incorporation of dopants in known amounts, with the additional benefits that the product is a powder which simplifies further processing. After calcination, the mesoscopic pores are accessible to big molecules, and up to 25% (by weight) of the cationic dye Janus Green B has been adsorbed from aqueous solutions. Possible bulk applications of mesostructured colloids include; the incorporation of active substances in mesoporous hosts intended for coatings applications, the coating of ink jet paper and the use of mesoporous materials as selective adsorbents in the purification of water.

P3.23

FORMATION STUDY OF NANOCOMPOSITE THIN FILMS OF NICKEL FERRITE DISPERSED IN A SILICA MATRIX PREPARED BY SOL-GEL PROCESS. Nelcy Della Santina Mohallem and Luciana Moreira Seara, Dept. of Chemistry, UFMG, Belo Horizonte, BRAZIL.

Atomic force microscopy was used to study the formation of nanocomposite thin films of nickel ferrites dispersed in a SiO_2 matrix prepared by sol-gel process. $\text{NiFe}_2\text{O}_4/\text{SiO}_2$ thin films were prepared using tetraethylorthosilicate (TEOS) as a precursor of silica, and ferric and nickel nitrate as precursors of the ferrite with 5 - 30% ferrite matrix contents. and deposited on glass, quartz and silicon plates using the dip-coating process. Thermal treatments were carried out at temperatures as high as 950°C , without breaking the films. The films obtained were adherent, transparent, homogeneous, and free of microcracks, with thickness between 70 and 100 nm. The nanocomposite films presented the formation of crystalline NiFe_2O_4 nanoparticles measuring between 6 and 10 nm dispersed in amorphous SiO_2 matrix and a saturation magnetization above 8 emu/g. The nanocomposite films obtained presented superparamagnetic behavior. We studied the organization of the nanoparticles in the films as a function of ferrite content and of annealing temperature by AFM, whose formation of islands is noted for 5 until 20% ferrite matrix contents. These formations ramify like aggregate fibers and only the films with 30% ferrite presented a homogeneous topography.

P3.24

SOL-GEL ELABORATION OF POROUS OXIDE COATINGS AS INTERPHASE IN SiC/SiC CERAMIC MATRIX COMPOSITES. M. Verdenelli, S. Parola, F. Chassagneux, S. Jacques, H. Vincent, J. Dazord, J.P. Scharff, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard Lyon 1, Villeurbanne, FRANCE; E. Bourgeat-Lami, Laboratoire de Chimie et Procédés de Polymérisation, UMR 140, ESCPE-Lyon, Villeurbanne, FRANCE.

Fibres reinforced Ceramic Matrix Composites (CMCs) are of great interest for applications under high thermal conditions or mechanical constraints (ex. vehicles, aerospace). The concept of porous oxide interphase for the deflection of matrix cracks has been known for several years. Several methods can be used to elaborate thin films on fibres, including Chemical Vapour Deposition (CVD), sputtering and the sol-gel process. Among the numerous advantages of the sol-gel process compared to conventional methods, the low temperature and the possibility to control the porosity by adding various templates were of a great interest for our purpose. The elaboration and characterization of oxide interphase with controlled porosity on Hi-Nicalon SiC fibres and their use in SiC/SiC composites will be reported. Interphases associating dense/porous/dense or porous/dense coatings will be discussed. The ionic surfactant cetyltrimethylammonium bromide $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$ (CTAB) or functionalised latex spheres were used as templates to create the porosities. Silica doped alumina systems were selected for their high temperature of crystallization and melting, in order to maintain the porosity even at high temperature. The SiC matrix was prepared by CVD using methyltrichlorosilane as the precursor. The characterisation of the systems, coatings and composites, using SEM, TEM and tensile tests will be presented.

P3.25

PERIODIC MESOPOROUS SiCO GLASSES WITH CUBIC SYMMETRY STABLE AT 1000°C . R. Blum, V. Goletto, B. Toury, F. Babonneau, Chimie de la Matière Condensée, UPMC, Paris, FRANCE.

The use of bis(silylated) precursors, $(\text{RO})_3\text{Si-X-Si}(\text{OR})_3$, in conjunction with surfactants allows the preparation of periodic mesoporous organosilicas (PMOs). The presence of Si-O and Si-C bonds in the framework makes them very suitable as precursors for porous oxycarbide glasses. Previous studies on sol-gel derived SiCO glasses have demonstrated the unique high temperature properties of these materials in terms of mechanical strength and chemical durability. Additionally, if these materials can exhibit a periodic

porous network, they can find applications as filters, catalysts or membranes operating in severe conditions. The challenge will thus be to convert PMOs in SiCO glasses without a total collapse of the porous network during the pyrolysis treatment under inert atmosphere. PMOs with 2D-hexagonal and cubic Pm3n structures have been prepared from bis(trialkoxysilyl)ethane and cetyltrimethylammonium bromide. The two samples have been pyrolyzed under Argon up to 1000°C, and the pyrolysis intermediates analyzed by X-ray diffraction using synchrotron radiation, multinuclear solid state NMR (²⁹Si, ¹³C and ¹H) and N₂ adsorption-desorption experiments. While the 2D-hexagonal structure collapses after pyrolysis at 800°C, with a total cleavage of the Si-C bonds, the cubic pm3n structure is retained after pyrolysis at 1000°C. The sample is a SiCO glass with mixed SiC_xO_{4-x} units (x=0,1,2) and a very large surface area of 730 m²/g. The mechanism for the organosilica-to-glass transformation will be discussed as well as the high temperature behavior of these glasses.

P3.26

ENCAPSULATION OF IBUPROFEN IN MESOPOROUS SILICAS FOR DRUG DELIVERY APPLICATIONS: A SOLID STATE NMR CHARACTERIZATION. F. Babonneau, L. Camus, N. Steunou, Chimie de la Matière Condensée, UPMC, Paris, FRANCE; A. Ramila, and M. Vallet-Regi, Departamento de Química Inorgánica y Bioinorgánica, Facultad de Farmacia, UCM, Madrid, SPAIN.

Mesoporous silicas have a capability for accepting and delivering organic compounds and thus to act as drug delivery systems. It has already been shown that ibuprofen molecules can be encapsulated with loading as high as 30 wt% in MCM-41 silicas, functionalized or not by amino groups. Interactions between the guest molecules and the host matrix have been investigated by solid state NMR. The ¹³C MAS-NMR single pulse or cross polarization spectra, as well as the ¹H MAS NMR spectra demonstrate an extremely high mobility of the ibuprofen molecules when the matrix is not functionalized, despite the presence of a carboxylic function in the ibuprofen molecules. This suggests that the molecules are certainly present as hydrophobic dimers in the pore channels. On the contrary when the silica surface is functionalized with amino groups, the ¹³C NMR response shows a strong restriction in mobility suggesting the existence of interactions between the amino groups and the carboxylic groups. In order to demonstrate this hypothesis, benzoic acid, which exhibits a similar behavior compared to ibuprofen when encapsulated, has been used as a model compound. The availability of benzoic acid with a ¹³C-fully enriched carboxylic group makes possible the use of ²⁹Si-¹³C double resonance techniques, whose preliminary results will also be discussed.

P3.27

NANOSTRUCTURED ORGANOMETALLIC CATALYSTS FOR GREEN CHEMISTRY SYNTHESIS. Qingyuan Hu, Eric Hampsey, Xianglin Ji, and Yunfeng Lu, Dept of Chemical Engineering, Tulane University, New Orleans, LA.

Green chemistry has received much attention because of the need to maintain a clean world and sustain a long-term economic growth. A notable development is to use water as solvent for organic reactions. In the present work, we synthesize mesoporous silica supported nanostructured organometallic catalysts for the organic reactions in aqueous media. Usually, these catalysts are prepared by chelating the metal ions (e.g. Ni, Pd, and Pt) with organic functional ligands covalently bonded to the pore surface of mesoporous silica. These mesoporous silica supports are prepared using sol-gel process and the co-assembly of silica and surfactants. The surfactants are then removed by solvent extraction or calcination under N₂ to create mesoporous silica supported catalysts. These catalysts have been characterized using FTIR, X-ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA), Brunauer-Emmett-Teller techniques (BET) and Transmission Electron Microscope (TEM). As synthesized catalysts shows excellent catalytic activity for many organic transformations in aqueous media.

P3.28

Abstract Withdrawn.

P3.29

PREPARATION OF MICRON TO SUB-MICRON SIZED MESOPOROUS SILICA PARTICLES USING HIGH ENERGY BALL MILLING. J. Eric Hampsey, Claudio DeCastro, Byron McCaughey, Donghai Wang, Brian Mitchell, and Yunfeng Lu, Tulane University, Dept of Chemical Engineering.

Nanostructured silica particles with diameters in the micron to sub-micron range are of great interest due to their applications in catalysis and nanocomposite materials. In order for these particles to be used in industry, a process must be developed to affordably produce these particles on a large scale. This paper reports on a high-energy ball milling process that has been employed to create

micron to sub-micron sized mesoporous silica particles starting from a silica xerogel prepared by a surfactant self-assembly sol-gel process. We have studied the effect of milling conditions such as milling media (e.g., zirconia, stainless steel, and steel centered nylon balls), milling time, the presence of surfactants on the particle sizes, particle size distribution, and pore structure. Results from transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen adsorption, and other characterization techniques demonstrate the feasibility of producing large quantities of mesostructured particles by a simple milling process.

SESSION P4: TEMPLATING AND SELF-ASSEMBLY SYNTHESIS

Wednesday Morning, April 23, 2003
Metropolitan III (Argent)

8:30 AM P4.1

NANOPATTERNED TEMPLATES FOR THE CONTROLLED GROWTH OF MOLECULAR NANOSTRUCTURES.

Federico Rosei^a, Y. Naitoh, M. Schunack, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, Physics Department and I-NANO, University of Aarhus, DENMARK; P. Jiang, A. Gourdon, and C. Joachim, CEMES-CNRS, Toulouse, FRANCE. ^aPresent Address: INRS-EMT, Univ. du Quebec, Varennes (QC) CANADA.

Ordering molecular building blocks into a suitable architecture at the nanoscale is very appealing for the development of future integrated nanoelectronics [1]. We used a large organic molecule, Lander [2] (C₉₀H₉₈), and investigated its adsorption properties its Self-Assembly on Cu(110) by Scanning Tunneling Microscopy (STM), in the temperature range 100 - 300 K. The Lander has a central polyaromatic molecular wire (conducting backbone), and four "spacer legs" (3,5-di-tert-butylphenyl) for isolation from the substrate. The four legs are imaged with 3 different conformations by STM. Manipulation experiments with the STM at low temperatures on isolated Lander molecules adsorbed on step edges reveal a restructuring of Cu steps [2]. These molecules act as templates on the nanoscale, reshaping portions of step edges into characteristic nanostructures. The structure's width is two atomic rows, corresponding to the distance between the spacer legs within the molecule. This process is thermally activated: repeating the same manipulation experiments on molecules adsorbed at low temperatures (150 K), no restructuring of the Cu step edges is found. In a second set of experiments, a clean Cu(110) surface was nanopatterned by oxygen chemisorption. By dosing a proper amount of O₂ at 350°C we obtained a superstructure with 2 nm wide Cu troughs aligned along the [001] direction, with a periodicity of about 5 nm. When Lander molecules are deposited on this template, they preferentially adsorb on bare Cu regions. By tuning molecular coverage in a controlled manner we obtained long rows of 1 D molecular nanostructures. This type of forced self-assembly opens new possibilities for ordering organic molecules on surfaces. References. [1] C. Joachim, J.K. Gimzewski and A. Aviram, Nature 408, 541 (2000). [2] F. Rosei et al., Organic molecules acting as templates on Metal Surfaces, Science 296, 328 (2002).

8:45 AM P4.2

SIMULTANEOUS SYNTHESIS AND SELF-ASSEMBLY OF MIXED SEMICONDUCTOR NANOCRYSTALLITES IN A CUBIC MESOPOROUS TITANIA MATRIX. Michael H. Bartl, Univ of California at Santa Barbara, Dept of Chemistry and Materials Dept, Santa Barbara, CA; Stefan P. Puls, Univ Muenster, Inst fuer Physikalische Chemie, Muenster, GERMANY; Jing Tang, Univ of California at Santa Barbara, Materials Dept, Santa Barbara, CA; Karen L. Frindell and Gernot Wirmsberger, Univ of California at Santa Barbara, Dept of Chemistry, Santa Barbara, CA; Hellmut Eckert, Univ Muenster, Inst fuer Physikalische Chemie, Muenster, GERMANY; Galen D. Stucky, Univ of California at Santa Barbara, Dept of Chemistry and Materials Dept, Santa Barbara, CA.

In the last years solar cells and photocatalysts based on low-cost nanocrystalline semiconductor oxides rather than on solid-state junction devices (often made of silicon) have gained much interest. Especially sensitized titania (anatase nanocrystallites) has shown to be an excellent n-type semiconductor candidate for such devices. While sensitization of titania usually is done in a step-by-step procedure by activating pre-made and patterned titania matrices with organic dyes or semiconductor nanoparticles, we present here a simple and fast sol-gel self-assembly approach to simultaneously synthesize and 3-dimensionally organize different semiconductor nanocrystallites (titania anatase, CdS, CdSe, ...) within a transparent cubic mesoporous titania thin film matrix. The synthesis and patterning of these nanocrystallites-activated thin films involves only a one-pot single dip-coating approach followed by a calcination step under varying gas atmospheres. The simultaneous presence of the different nanocrystallites is confirmed by x-ray diffraction analysis as well as transmission electron microscopy and optical spectroscopy.

Furthermore, we present photocurrent and photovoltage data of these all-inorganic self-assembled mixed semiconductor nanocrystallite composites, which demonstrate that indeed the smaller band-gap semiconductor nanocrystallites (CdS, CdSe, ...) efficiently sensitize the larger band semiconductor (titania anatase).

9:00 AM *P4.3

THE FUNDAMENTAL OF SELF-ASSEMBLY CONTROLLED BY EVAPORATION IN THIN FILM PROCESSING. David Grosso, Florence Cagnol, Galo J. de A.A. Soler-Illia, Eduardo L. Crepaldi, Clément Sanchez, University Pierre et Marie Curie, Laboratoire Chimie de la Matière Condensée, Paris, FRANCE.

The Evaporation Induced Self Assembly (EISA) method has proven to be well-appropriated to the preparation of well-ordered mesoporous silica based films and has recently been extended to non-silica films. During liquid deposition, a thin layer of isotropic solution containing both the inorganic precursor and the templating surfactant is dragged on the substrate and the fast evaporation of volatile species drives the self assembly and the condensation to take place. The in-situ time-resolved investigations of such mechanism by 2D-SAXS has been applied to the following well-reproducible systems: (i) Tri-dimensional cubic (Pm3n) and (Im3n), bi-dimensional (p6m) and hexagonal (P63/mmc) SiO₂ films. (ii) (p6m) and (Im3n) TiO₂, ZrO₂, ZrO₂-Y₂O₃, Al₂O₃ and V₂O₅ films. (iii) (Pm3n) and (p6m) organically modified well-organised silica films from R-Si(OEt)₃ precursors (R = Me, Phenyl, Pyrrol, amino and phosphine groups, etc). The active organic molecules been successively grafted in the network pores by "one-pot" synthesis. These investigations showed that self-organisation is a complex process that involves several steps and is governed by various critical parameters that are related to the nature of the inorganic precursor (e.g. silica, non-silica, modified silica), to the nature of the surfactant (e.g. ionic, non-ionic), to the sol-gel conditions (e.g., pH, ageing time, etc), and also to the processing conditions (e.g. Relative Humidity). Through these, we will demonstrate that a Modulable Steady State (MSS) exists, during which the final film mesostructure can be modulated by adjusting the critical parameters such as the relative humidity. A qualitative model, related to "phase diagrams", will be proposed to explain the formation of these evaporated materials.

9:30 AM *P4.4

NEW ELECTRONIC AND STRUCTURAL MATERIALS THROUGH INORGANIC/SURFACTANT CO-ORGANIZATION. Sarah H. Tolbert, Dong Sun, Andrew E. Riley, Bradley L. Kirsch, and Junjun Wu, UCLA, Department of Chemistry and Biochemistry, Los Angeles, CA.

The first part of this talk will focus on the formation of new electronic materials through inorganic/surfactant co-assembly. In this work we use Zintl clusters, reduced main group clusters, as building blocks for new semiconducting materials. Using the examples of pure Ge and a variety of metal tin telluride alloys, we show that semiconductor/surfactant composites and periodic nanoporous semiconductors can be synthesized using the ideas of electrostatically driven self-organization. In the talk, we first explore the structure of these materials, characterizing their properties on both that atomic and nanometer length scales. We then explore the optical and electronic properties of these narrow band gap semiconductors and show how these properties can be tuned by changing size, surface structure, or chemical composition. For the second part of the talk, we examine how the well-defined nanometer scale periodicity of templated inorganic materials can affect their mechanical properties. In particular, we explore the properties of hexagonal silica/polymer films under tension with a goal of understanding how the nanometer scale architecture of the composite affects the elastic properties of the material.

10:30 AM *P4.5

SELF-ASSEMBLED NANOSTRUCTURES IN DESIGNED SPACES. Thomas Bein, Kathleen Hoekstra, Svetlana Mintova, Nikolay Petkov, Jake Reeder.

Porous materials with nanoscale channels are versatile structural templates for a multitude of functional guests. The generation of channel structures with controlled morphology such as oriented films often requires the use of novel strategies such as self-assembly, non-covalent interactions, host-guest chemistry, and structural templates. We will discuss key aspects of this approach, including the growth of oriented channel structures on substrates and inclusion chemistry using the nanoporous hosts as templates. Nanoscale zeolites are being used as building blocks for the seeded growth of thin microporous films with controlled crystal orientation. Another approach is the controlled growth of zeolites on molecularly functionalized surfaces. In an effort to extend the scale of the oriented channel systems, we have recently developed a method for the production of nanoporous micelle-templated silica films with

accessible, vertically-aligned one-dimensional pore structures, using an electric field. The above microporous and mesoporous hosts in the form of bulk and thin films are being employed as structural templates for the synthesis and stabilization of molecular guests such as dyes, or of nanometer scale conducting structures such as conducting polymers, charge-transfer salts, and carbon filaments. These systems can serve as models for the construction of more complex nanoscale conducting networks built with self-assembly techniques.

11:00 AM P4.6

TEMPLATELESS SELF-ASSEMBLY OF NANOWIRE CAGES. A.V. Ellis, J. D'Arcy-Gall, R. Goswami, P.G. Ganesan, and G. Ramanath, Rensselaer Polytechnic Institute, Materials Science and Engineering Dept, Troy, NY.

We describe and demonstrate a new, simple, low-temperature, template-less approach to create highly porous, cocoon-shaped three-dimensional cages comprised of fractal networks of interwoven Au nanowires. Such high-surface area meso-scale superstructures would be attractive for applications such as catalysis and sensing, and serve as templates for molecular separation and assembly. Our approach is a completely new adaptation of the Brust method and involves the coalescence of nanoclusters created from two-phase mixtures into nanowired superstructures without the use of phase transfer agents. Scanning and transmission electron microscopy (SEM and TEM) measurements show that nanocage dimensions are uniform, and range from approximately 200 nm to several microns, depending on the synthesis parameters. The constituent nanowires have a uniform diameter of approximately 5-10 nm, and consist of fcc polycrystals. By adjusting the pH, and varying the solvent chemistry and process-step time-intervals, we can control the nanostructure size, shape, and yield, and tune morphologies from isolated nanoparticles, to nanowires, to interwoven 2D and 3D nanowire-networks. Preliminary X-ray photoelectron spectroscopy and Raman spectroscopy results indicate that the nanostructures are hydrophobically passivated. Based upon the above, we propose a model involving liquid/liquid interfacial chemistry and nanocluster surface charge to explain nanowire formation and nanocage assembly in biphasic media.

11:15 AM P4.7

TEMPLATING SYNTHESIS OF HIERARCHICAL NANOWIRE AND NANOMESH THIN FILMS. Donghai Wang, Weilie L. Zhou, Byron F. McCaughy, J. Eric Hampsey, Xianglin Ji, Ying-Bing Jiang, Huifang Xu, Jinke Tang, Russell H. Schmehl, Charles O'Connor, C. Jeffrey Brinker, and Yunfeng Lu.

Nanostructured thin films composed of metal or semiconductor nanowires or nanomeshes have been fabricated via electrodeposition techniques using mesoporous silica thin films as templates. This method continually grows metal or semiconductor within the pore channels of the templates from the bottom conductive substrate upward till the mesoporous channels are filled, providing a ready and efficient route to fabricate macroscopic hierarchical nanowires or nanomeshes thin films. The structures of the nanostructured thin films have been characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), and electron energy-loss spectroscopy (EELS), and other techniques. Our results indicate that it is possible to control mesostructure of the nanowires and nanomeshes by controlling the pore structure of the templates. This provides a new fabricating technique to synthesize nanostructured metallic and semiconductor thin films for fuel cell, electrodes, optical hosts, catalyst, magnetic materials, photovoltaics, sensors, and other applications.

11:30 AM P4.8

NANOWIRE AND NANOTUBE SYNTHESSES THROUGH SELF-ASSEMBLED NANOPOROUS AAO TEMPLATES. H. Hau Wang, Catherine Y. Han, Zhili L. Xiao, Gerold A. Willing, Urs Geiser, Ulrich Welp, Vitalii K. Vlasko-Vlasov, Wai K. Kwok, Samuel D. Bader, and George W. Crabtree, Materials Science Division, Argonne National Laboratory, Argonne, IL.

Nanowires and nanotubes have attracted significant interest during recent years due to their novel electrical, magnetic, and photonic properties. Quantum confinement, proximity interaction, and surface plasmon enhancement effects are among a few unique phenomena associated with these materials. A convenient procedure to prepare these materials is through anodized aluminum oxide (AAO) template synthesis. Nanoporous AAO membranes with pore diameters ranging from 30 to 200 nm can be prepared with anodization in oxalic, sulfuric and phosphoric acids under various reaction conditions. With repeated anodization-etching cycles, highly ordered straight channels can be prepared through self-organization. With electro- and electroless deposition, a variety of nanowires and nanotubes such as Ni, Co, Au, Pb, PbO₂, Bi, etc. have been prepared. The synthesis, characterization, and physical properties of these materials will be

presented. Work at ANL is supported by the US DOE/BES Materials Science under contract W-31-109-ENG-38.

11:45 AM P4.9

MIXED SURFACTANT LIQUID CRYSTAL TEMPLATES FOR PLATINUM AND PALLADIUM NANOTUBES. Tsuyoshi Kijima, Takumi Yoshimura, Masafumi Uota, Takayuki Ikeda, Shinji Mohri, Shinji Uoyama, Miyazaki University, Department of Applied Chemistry, Miyazaki, JAPAN.

Since the discovery of mesoporous silicas MCM-41 the surfactant-templating approach has been extensively applied to the synthesis of a great number of nanoporous or nanotubular inorganic materials for their wide use in catalysis, separation technology, and microelectronics. The previous syntheses have unexceptionally used a single surfactant, ionic or nonionic, in contrast to a general use of mixed surfactant systems in industrial processes. Furthermore, none has been described on the synthesis of noble metal free nanotubes of less than ten-nanometer diameter, although a variety of nanoporous metals have been fabricated using various templates. This paper reports the first synthesis of platinum nanotubes with inner and outer diameters 3 and 6 nm, respectively, by a novel strategic approach which involves the reduction of platinum species confined to the lyotropic mixed liquid crystals of two nonionic surfactants as a template. Palladium nanotubes with nearly the same size were also obtainable in a similar procedure. The uniformly sized platinum nanotubes were synthesized typically by cooling an aqueous mixed solution of hexachloroplatinic acid, nonaethyleneglycol monododecyl ether and polyoxyethylene sorbitan monostearate and then reducing the resulting liquid crystalline phase with hydrazine at 25°C. The precursory liquid crystals gave a XRD pattern characterized by a definite peak with $d=6.32$ nm corresponding to the 100 reflection for a hexagonal phase with $a=7.37$ nm. We thus propose that the two differently sized surfactant molecules form a hexagonal assembly of double-cylindrical mixed micelles in which platinum or palladium species are reduced to grow into nanotubular metals within the cylindrical space. The present platinum and palladium nanotubes are promising for potential application as electrodes in batteries and fuel cells, catalysts for purification of exhaust gas and electronic nanodevices. The mixed surfactant templating method would serve to fabricate a much wider range of nanotubular materials, inorganic or organic, than previous approaches.

SESSION P5: SELF-ASSEMBLED BIOLOGICAL
AND BIOMIMETIC SYSTEMS
Wednesday Afternoon, April 23, 2003
Metropolitan III (Argent)

1:30 PM P5.1

S-LAYER PROTEINS AS BASIC BUILDING BLOCKS IN A BIOMOLECULAR CONSTRUCTION KIT. Dietmar Pum, Erika Gyoervary, Bernhard Schuster, Uwe B. Sleytr, Center for Ultrastructure Research, Universitaet fuer Bodenkultur, Vienna, AUSTRIA.

The study of biological self-assembly systems is a new and rapidly growing scientific and engineering field that crosses the boundaries of existing disciplines. The attractiveness of such bottom up processes lies in their capability to build uniform, ultrasmall functional units and the possibility to exploit such structures at meso- and macroscopic scale. In this context, two-dimensional bacterial surface layer proteins (S-layer proteins) represent very versatile assembly systems with unique features as structural basis for a complete supramolecular construction kit, involving all major species of biological macromolecules (proteins, lipids, glycans, and nucleic acids). S-layers are the most commonly observed cell surface structures in prokaryotic organisms (bacteria and archaea). They are composed of a single protein or glycoprotein species (Mw = 40 to 200 kDa) and exhibit either oblique, square or hexagonal lattice symmetry with unit cell dimensions in the range of 3 to 30 nm. S-layers are generally 5 to 10 nm thick. They represent highly porous protein meshworks with pores of uniform size and morphology in the 2 to 8 nm range. One of the key features of isolated S-layer proteins is their intrinsic tendency to self-assemble into two-dimensional arrays in suspension and at various interfaces. The wealth of information accumulated on the general principles of S-layers led to a broad spectrum of potential applications in many areas of both life and materials sciences. The possibility to change the natural properties of S-layer proteins by genetic manipulation opens a new horizon for the tuning of their structural and functional features. Functionalized S-layer proteins that maintain their propensity for self-assembly have led to new affinity matrices, diagnostic tools, vaccines, or biocompatible surfaces, as well as to biological templating or specific biomineralisation strategies at surfaces.

1:45 PM P5.2

APPLICATION OF NANOMATERIALS BY SELF-ASSEMBLED VIRUS PROTEIN. Yongquan Shen Yongquan and Huajian Gao, Max-Planck Institute for Metals Research, Dept. of Theory of Mesoscopic Phenomena, Stuttgart, GERMANY; Rolf E. Streeck and Martin Sapp, Mainz University, Institute for Medical Microbiology, Mainz, GERMANY.

Self-assembled nanostructured materials can be used for the encapsulation of guest molecules, with potential applications in gene transfer and drug delivery. The protein coats of viruses (virions) commonly comprise hundreds of subunits that self-assemble into particles for transporting viral nucleic acids. Many virions can undergo reversible structural changes that allow exogenous molecules access to their interior. The human papillomas viruses (HPV) are 50-60 nm in diameter as measured by electron microscopy. The viruses shell is composed of 360 identical major capsid protein together with 12 identical minor capsid protein arranged on an icosahedral lattice. In this study, HPV was used as a model system for reversible entrapment of DNA molecules. HPV33 capsid proteins were expressed and self-assembled into virus like particles (VLPs) in insect cells using baculovirus expression system. HPV33 VLPs were purified with two step CsCl gradients ultracentrifuge. Purified HPV33 VLPs can be detected 50nm in diameter under electron microscopy. 10ug of purified VLPs were disassembled at 20mM DTT, then mixed with 1ug of pEGFP plasmids DNA and reassembled with dilution up to 5mM of CaCl₂ at final concentration. The disassembly-reassembly process can be monitored via VLPs structure change with electron microscopy. The infection assays indicated DNA molecules can be packaged into empty VLPs in the disassembly-reassembly process. This approach to encapsulation macromolecules has provided a versatile strategy for materials synthesis and molecular entrapment as well as some application to the formation of other nanoscale materials.

2:00 PM *P5.3

ORGANIC-BRIDGED MESOPOROUS MATERIALS POSSESSING HIERARCHICALLY ORDERED STRUCTURES IN MESO- AND MOLECULAR SCALES. Shinji Inagaki, Guan Shiyou, Mahendra P. Kapoor, Qihua Yang, Toyota Central R&D Labs., Inc., Aichi, JAPAN.

We reported the synthesis of the mesoporous benzene-silica hybrid possessing crystal-like ordered structure in the pore walls. The mesoporous material has unique pore-surface structure in which hydrophobic benzene and hydrophilic silicate layers are arranged alternatively with a 7.6 Å periodicity. The novel mesoporous material is expected to exhibit highly selective and active catalysis and opto-electrical efficiency because the molecular-scale periodicity in the walls could enable structure orientation of guest molecules or clusters enclosed in the pores. The mesoporous benzene-silica was synthesized by condensation of 100 % of 1,4-bis(triethoxysilyl)benzene [(C₂H₅O)₃Si-C₆H₄-Si(OC₂H₅)₃, BTEB] in the presence of octadecyltrimethylammonium chloride surfactant under basic condition. Here, we report successful extension of the unique ordered pore-wall system for the other organic-bridged mesoporous including biphenyl (-C₆H₄-C₆H₄-), 1,3-benzene and ethylene (-CH=CH-). The periodicities in the walls were 11.72, 7.64 and 5.6 Å for biphenyl, 1,3-benzene and ethylene, respectively. The periodicity increased with increasing molecular length of organic groups, suggesting the validity of the lamellar structure with the organics as a pillar of the walls. This indicates that strong hydrophobicity (or interaction) of organic groups is important to induce the organization of organosilane molecules to lamellar structure in the walls. The molecular-scale periodicity was not observed for the amorphous benzene-silica and other organic-inorganic hybrid materials produced by sol-gel methods without using surfactants. This suggests that the self-assembly of the surfactant and the resulting mesostructure promote the formation of the molecular-scale periodic structure.

2:30 PM P5.4

BIO-INSPIRED SUBMICRON ELECTRODES. Ivan Stanish and Alok Singh, NRL, Center for Bio/Molecular Science and Engineering, Washington, DC; Daniel Lowy, Nova Research, Inc. Alexandria, VA.

Immobilized polymerized electroactive vesicles (IPEVs) are submicron biocapsules capable of storing charge in confined environments and chemisorbing on surfaces. Methods to immobilize stable submicron sized electroactive vesicles and the means to measure electroactivity of IPEVs at nanolevels have been demonstrated. IPEVs can withstand steep potential gradients applied across their membrane, maintain their structural integrity against surfaces poised at high/low electrical potentials, retain electroactive material over several days, and reversibly mediate (within the membrane) electron flow between an electrode surface and the vesicle interior. IPEVs have the potential to be used for charge storage and electron coupling applications that operate on the submicron scale and smaller.

2:45 PM P5.5

ENCAPSULATION OF BIOMOLECULES VIA VESICLES FORMED FROM HEADGROUP POLYMERIZABLE DIACYL-PHOSPHOETHANOLAMINE PHOSPHOLIPIDS. Glenn E. Lawson and Alok Singh, Naval Research Laboratory, Center for Bio/Molecular Science and Engineering, Washington, DC.

Polymerized vesicles offer a simple and effective solution for encapsulation of bioactive molecules or molecular aggregates and provide control over their release properties. With a goal to produce vesicles resistant to physical, mechanical and chemical perturbation, synthesis of four, novel headgroup polymerizable phospholipids have been prepared by reacting 1,2-diacyl-sn-glycero-3-phosphoethanolamines (acyl chains containing 12, 16 or 18 carbon atoms) with photosensitive monomers (such as aromatic hydrocarbons). The encapsulation, permeability and stability studies on the vesicles were performed before and after polymerization followed by freeze drying and redispersion steps. Unlike their phosphocholine analogs vesicle formation from these phospholipids has been greatly influenced by the nature of the dispersion medium as indicated by calorimetric studies and the polymerization behavior of the vesicles. We will present our studies on the formation and stability of the polymerized vesicles using various perturbations including organic solvents and the retention properties of the vesicles with encapsulated bioactive molecules (such as piroxicam) and macromolecules (such as glucose oxidase).

3:30 PM *P5.6

BIOMIMETIC SYNTHESIS OF SILICA NANO- AND MICROSTRUCTURES. Peter Behrens, Gallus Schechner, Petra Bärnreuther, Ilka Krüger, Institut fuer Anorganische Chemie, Universitaet Hannover, Hannover, GERMANY.

A specific characteristic of biominerals is their hierarchical structure, comprising the spatial organization on several length scales. Biomineralisation processes take place under physiological conditions, i.e. at temperatures between 4 and 37°C and at pH-values around 7. Peptides, proteins and polysaccharides as well as simpler bioorganic macromolecules are involved in the biomineralization of silica, with one of the more obvious roles being that of a structural template. We have used alkyl--glucosides, i.e. non-ionic amphiphilic molecules ("sugar surfactants"), as structure-directing agents to control the structural evolution of amorphous silica in a sol-gel process carried out at or near to physiological conditions. The syntheses lead to hierarchically ordered composite materials with unusual morphologies, which resemble the micrometer structures of biominerals. This includes for example regular networks as found in glass sponges as well as the formation of honeycomb patterns and spikes similar to those found in diatoms. After removal of the organic component, nanoporous materials are obtained, with properties similar to those of M41S mesoporous materials. The fact that such complex morphologies can be formed in a simple synthesis system lends credit to the idea that the formation of the intricate structures of natural biosilicas does not necessarily involve a strict control of all steps of the aggregation, but may rather rely on less strictly controlled self-aggregation processes.

4:00 PM *P5.7

SPONTANEOUS HIERARCHICAL GROWTH, PATTERNING, AND ALIGNMENT OF SELF-ASSEMBLY MATERIALS. Jun Liu, Zhengrong R. Tian, James A. Voigt, Sandia National Laboratories, Albuquerque, NM.

Biomaterials like seashells and diatoms display rich morphologies and multiple scale ordering. One of the challenges for self-assembled nanoscale materials is the assembly, patterning, and alignment of large objects for device applications. This presentation will discuss a novel hierarchical and self-similar crystal growth process leading to spontaneous formation of large objects with controlled morphology and ordering from nano- to macro-scale. Well-defined octahedral crystals were formed from the cubic mesophase silicate through controlled nucleation and growth. These microscopic polyhedral mesophase crystals were used as the fundamental building blocks to assemble large ordered crystals and open structures preserving the orientation and morphology of the building blocks. A wide range of controlled morphologies was derived through different stacking of the primary crystals. Furthermore, we will discuss the effect of surface chemistry, and methods for three-dimensional alignment and patterning of the self-assembled cubic structures. The methods discussed for self-assembled silicates are also applied to other oxide materials.

4:30 PM P5.8

FIBROUS CALCIUM CARBONATE. M.J. Olszta, J. Thiel, C. Cox, S. Gajjaraman, L.B. Gower, University of Florida, Department of Materials Science and Engineering, Gainesville, FL.

Fibrous crystalline growths are abundant in biominerals, ranging from vertebrates (e.g. enamel layer in mammals composed of rods or fibers of calcium phosphate (CaP)) to invertebrates (e.g. keel region of sea urchin teeth). The 3.5 - 7.0 μm diameter crystalline growths, embedded in an amorphous calcium carbonate matrix in the keel region of the sea urchin tooth, are composed of single crystalline magnesium bearing calcite. These smooth crystalline structures seem contradictory to classical crystal growth, which yields faceted crystals expressing lower energy crystalline planes. Using a polymer-induced liquid-precursor (PILP) process, we have grown single-crystalline calcite fibers with diameters on the order of 0.5 μm and lengths varying from 5 - 40 μm . These fibers grow off of seed crystals ranging from 20 - 40 μm in diameter, grown using a vapor diffusion process, to 0.5 mm in diameter, synthesized using a gel method. Mg^{2+} and Sr^{2+} ions were added at ratios of 50:1 Ca:Mg or 50:1 Ca:Sr to the crystallizing solution to facilitate growth of these fibers. Under polarized optical microscopy the fibers display a single crystalline extinction pattern. If these non-equilibrium morphologies remain in solution, they tend to succumb to surface re-organization, forming iso-oriented microfacets on the fiber. A single crystalline pattern is also seen for these fibers with electron diffraction. While the exact mechanism for fiber growth is not yet understood, it appears to be related to the fluidic nature of the mineral precursor phase, which may preferentially accumulate at the growing tip of the fiber, analogous to nanofiber formation via vapor phase technologies.

4:45 PM P5.9

SURFACTANT TEMPLATED COMPOSITES OF CALCIUM PHOSPHATE WITH DIVERSE INTRICATE MORPHOLOGIES. Sajanikumari Sadasivan^a, Deepa Khushalani^b, Stephen Mann^a.
^aSchool of Chemistry, University of Bristol, UNITED KINGDOM; ^bSchool of Physical Sciences, University of Kent, Canterbury, Kent, UNITED KINGDOM.

Hybrid composites of calcium phosphates have attracted interest in recent years as biomaterials because of their excellent biocompatibility. In the human body calcium phosphate exists in different morphologies ranging from mineralised collagen fibrils in bone to needle like crystal rods in enamel. Whatever the form, calcium phosphate is arranged in a very organised manner. Hence, to mimic the different morphologies while maintaining the supramolecular arrangement is a challenging aspect of biomaterial chemistry. In the present work we have developed a surfactant templated synthesis of composite calcium phosphate with various morphologies. The product obtained had diverse morphologies ranging from nanofilaments arranged in a lamellar manner to nanofibrils extending from a central core. The different structures could be obtained exclusively by slight alteration in the synthesis condition. Triblock copolymer (P123) was used as a surfactant while a hydrophobic calcium salt behaved as a calcium precursor and as a cosurfactant. A more comprehensive study was done on the nanofilaments arranged at a constant distance from each other. The products were analysed by TEM, SEM, TGA and FTIR spectroscopy.

SESSION P6: POSTER SESSION
SELF-ASSEMBLY, TEMPLATING AND
BIOMIMETIC SYNTHESSES
Wednesday Evening, April 23, 2003
8:00 PM
Golden Gate (Marriott)

P6.1

NUCLEATION AND SELF-ASSEMBLY OF ULTRATHIN IRON OXIDE FILMS ON A Ru(0001) SUBSTRATE. Guido Ketteler and Wolfgang Ranke, Dept of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Berlin, GERMANY.

Heteroepitaxial growth of ultrathin iron oxide films and iron oxide nanostructures on a Ru(0001) substrate is investigated by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Metastable FeO(111) layers grow with a thickness up to 4 monolayers (ML) on Ru(0001) by oxidation of the corresponding amount of Fe in 10^{-6} mbar O_2 at 870 K with a final anneal to 1000 K. These films have strongly expanded lattice constants and form specific coincidence structures with the Ru(0001) substrate. Prolonged oxidation transforms the whole film to the thermodynamically more stable $\text{Fe}_3\text{O}_3(111)$ phase. This phase transition requires at least two bulk repeat units of $\text{Fe}_3\text{O}_3(111)$ and does therefore not occur in very thin FeO(111) films. Oxidation of 1-3 ML thick FeO(111) films leads to a heterogenous nucleation of $\text{Fe}_3\text{O}_3(111)$ islands, preferentially at step edges. Homogenous nucleation of self-assembled, periodic $\text{Fe}_3\text{O}_3(111)$ nanodomains with diameters of $\sim 2\text{-}3\text{nm}$ embedded in an ultrathin FeO(111) occurs in ~ 4 ML thick FeO(111) films. The driving force is the electrostatic energy gain and an energy gain associated with the exothermic phase transition to Fe_3O_3 . These nanostructures represent a promising candidate for the realization of

quantum magnetic disks. Further oxidation causes these domains to grow and finally coalesce into a closed $\text{Fe}_3\text{O}_3(111)$ film. The growth and phase transitions of iron oxide film structures are compared to the previously investigated Stranski-Krastanov growth of iron oxide films on Pt(111) [W. Weiss, M. Ritter, Phys. Rev. B59 (1999), 5201]. Differences in the growth behaviour of iron oxides on different substrates are discussed in terms of the different affinity of the iron oxide film towards the substrate material showing that the stabilization mechanism and growth mode for the same metal oxide phases depends strongly on the interfacial interaction.

P6.2
IMMOBILIZATION OF PROTEINS IN THE ORGANICALLY FUNCTIONALIZED MAGNESIUM PHYLLOSILICATE CLAY MATRIX. Avinash Patil, Eswaremoorthy Muthusamy, Stephen Mann, School of Chemistry, University of Bristol, UNITED KINGDOM.

Ordered inorganic-organic lamellar materials with structures analogous to 2:1 trioctahedral phyllosilicates with approximate compositions $\text{Mg}_6\text{Si}_8\text{R}^1_x\text{R}^2_{8-x}\text{O}_{16}(\text{OH})_4$ (where R^1 and R^2 is hexdecyltrimethoxysilane (HD) and 3-aminopropyltriethoxysilane (APTES) have been synthesized and characterized by XRD, IR, TGA and chemical analysis. These materials consists of pendent organic functionalities covalently attached to the inorganic framework. The application of these layered modified magnesium phyllosilicate clays for the immobilization of heme proteins such as myoglobin (Mb), haemoglobin (Hb) and cytochrome-c (Cytc) into their galleries/surfaces were studied under mild conditions (pH 8-9, room temperature). The immobilized proteins retained their structure and activity. FTIR and UV-Visible absorption spectroscopy studies clearly suggest that proteins have preserved total structure and heme group. The redox activity and reversible binding of CO over reduced clay-protein composites was investigated from the shift of the Soret band (407 nm) by UV-Visible absorption spectroscopy. The stability of the immobilized proteins with respect to high pH, temperature was also compared with the free protein. From our studies it was found that organically functionalized magnesium organophyllosilicates provide a robust environment for the accommodation of fragile biomolecules with intact biochemical activity. These novel biocompatible materials can be extended as host materials for the entrapping range of a biomolecules for use in biocatalysis, biosensor and biodiagnostic applications.

P6.3
Abstract Withdrawn.

P6.4
HIGH SURFACE AREA MESOPOROUS ARAGONITE PERPARED FROM SURFACTANT-STABILIZED AMORPHOUS CALCIUM CARBONATE NANOPARTICLES IN REVERSE MICRO-EMULSIONS. Mei Li^a, Benedicte Lebeau^b and Stephen Mann^a.
^aSchool of Chemistry, University of Bristol, UNITED KINGDOM;
^bLaboratoire de Materiaux Mineraux, UMR 7016 CNRS, ENSCMu-UHA, Mulhouse-FRANCE.

The water-induced crystallization of alkylbenzenesulfonate-coated amorphous calcium carbonate (ACC) nanoparticles in water-in-isooctane NaOT microemulsions at $w = 20$ produces aragonite nanocrystals (10 - 20 nm) that self-assemble with surfactants into a mesoporous structure with doughnut-like shape and high BET surface area (112m²/g). The nanoparticles are single crystals and crystallographically continuous such that the torus-shaped particles are mosaics with preferential alignment normal to the [001] direction. The formation of aragonite-surfactant hybrid mesoporous structures depends on the water content inside the microemulsion droplets ($w = 18 - 22$) and the time of the transformation (5 hours). The results indicate that crystallization of aragonite involves initial crystallization of the surfactant-stabilized ACC precursor clusters to vaterite followed by transformation to the aragonite mesoporous structure. The surfactants could be removed from the aragonite-surfactant hybrid material by washing to produce the mesoporous inorganic replica.

P6.5
Abstract Withdrawn.

P6.6
POROUS NANOWIRES BASED ON DIRECTED ASSEMBLY. Feng Li, Lianbin Xu, Weilie Zhou, Jibao He, John B. Wiley, University of New Orleans, Advanced Materials Research Institute and the Department of Chemistry, New Orleans, LA.

Anodic alumina membranes can be used as templates to produce porous nanowire arrays. The control of size of the nanowires, combined with self-assembly techniques, can lead to interesting extended structures. The novel 1-D systems may be important to the development of new 1-D reverse photonic crystal.

P6.7
Abstract Withdrawn.

P6.8
SELF-ASSEMBLED ALUMINA PORE FORMATION ON NANOPATTERNED ALUMINUM SURFACES. Kornelius Nielsch, Joy Cheng, and C.A. Ross, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA; Jinsub Choi, Ralf B. Wehrspohn, and Ulrich Gösele, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

In the recent years, self-ordered alumina pore channel arrays, based on an approach of Masuda et al. [1], have attracted a lot of interest as a template material for the synthesis of anisotropic nanoparticles with a defined diameter ($\pm 10\%$). In analogy to polycrystallites, the pore channels are hexagonally self-arranged in domains. In these pore arrays, numerous lattice defects and domain boundaries exist where large deviations of the average pore diameter occurs. Recently, it has been demonstrated by J. Choi et al. [2] that a monocrystalline arrangement on a cm²-scale can be obtained by using imprint lithography. In this case for each pore channel a small pit as a nucleation site was created on the Al surface. In this paper, we want to analyze the influence of the patterned Al surfaces on the formation of porous alumina in general. A topographically modulated Al surface with a periodicity between 200 and 500 nm was achieved by imprinting SiO₂-grating structures in aluminium substrates. Subsequently, the pre-patterned surfaces were anodized in phosphoric acid or oxalic acid. An enormous improvement in the pore arrangement was observed, when the periodicity of the grating structure is $\lambda = 0.86 \times N \times D_{INT}$ ($N = 0.5, 1, 1.5, 2, \dots$; D_{INT} = inter-pore distance) or $\lambda \approx 2.16 \times N \times U_{ox}$ (U_{ox} = Oxidation potential). According to the grating lines the whole pore channel array can be arranged in the same orientation without grain boundaries but numerous lattice defects are still observed. Additionally, we will show results from the anodization of Al substrates with modulated topographies in two-dimensions. The concept of guiding the self-assembly process during the growth of porous alumina by lithographic patterning with a feature size $\gg D_{INT}$ is very promising for the rapid, inexpensive and large scale synthesis of very monodisperse nanowires in length and diameter. [1] H. Masuda and K. Fukuda, *Science* **268**, 1466, (1995). [2] J. Choi et al., *MRS Symp. Proc.* **722**, L5.2, (2002).

P6.9
FABRICATION OF MONODISPERSE SILVER NANOWIRES EMBEDDED IN MONODOMAIN POROUS ALUMINA TEMPLATES ON A cm²-SCALE. Jinsub Choi^a, Guido Sauer^b, Kornelius Nielsch^a, Ralf B. Wehrspohn^a, and Ulrich Gösele^a; ^aMax Planck Institute of Microstructure Physics, Weinberg Halle, GERMANY; ^bInstitute of Physical and Theoretical Chemistry, University Erlangen-Nuremberg, Erlangen, GERMANY.

Monodomain porous alumina templates with 500 nm inter-pore distance, 100 μm length and adjustable pore diameters were fabricated via indentation by a master stamp consisting of hexagonal pyramids of Si_3N_4 with 500 nm lattice constant, subsequent anodization under proper conditions and a widening process in phosphoric acid after anodization. Afterwards, monodisperse silver nanowires with a high aspect ratio were synthesized via electrochemical plating into the monodomain porous alumina template. Monodispersity of the silver nanowires embedded in the alumina template is about 2%. After removing the templates, free standing silver nanowires with 20 \sim 30 μm lengths were achieved. It was also possible to use thin aluminum film sputtered on Si substrates for this process. This allows to fabricate silver nanowire arrays on Si. In both cases, a nearly 100% pore filling was obtained. Moreover, we will show hierarchically ordered porous alumina with about 25 to 40 nm pore diameter on one side and 180 nm pore diameter on the other side, yielding branched silver nanowires.

P6.10
CARBON NANOTUBE WITH VARIOUS NANOSTRUCTURES. Wansoo Huh, Soongsil University, Seoul, KOREA; Barry Farmer and Richard Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate MLBP, Wright-Patterson AFB, OH; Don Shiffler, AFRL/DE, Kirtland AFB, NM.

Many current synthesis methods yield carbon nanotubes (CNT) with irregular size, broad size distribution, and impurities, compromising some practical applications of CNTs. For CNT applications ranging from devices to nanocomposites, it is desirable to fabricate CNTs with controlled external diameter, internal pore size and length. Controlled anodization of aluminum oxide is used to provide templates, enabling fabrication of CNTs with prescribed dimensions. After electrodeposition of Co catalyst inside the template pores, carbon nanotubes with uniform diameter and uniform length was achieved

using acetylene, hydrogen, and argon gas in thermal CVD process. In addition, judicious selection of anodization parameters gives bidirectional pore formation as well as unidirectional pores in template. This may enable us to synthesize various shapes of two dimensional carbon nanotube with a broad range of mechanical properties, electrical conductivity, and thermal conductivity.

P6.11

FABRICATION OF OXIDE NANO HOLE ARRAY AND THEIR APPLICATIONS. Shinsuke Yamanaka, Tsuyoshi Hamaguchi, Masayoshi Uno, Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Osaka, JAPAN.

A variety of oxide nanohole arrays have been prepared from an aqueous solution process. The chemical process used in the present study is simple and green, and any special equipment such as a vacuum system, a temperature controller or potentiostat is not required for the process. An anodic alumina was immersed in a metal-fluoro complex solution at room temperature and a few hours immersion enabled us to obtain the nanohole arrays of oxides such as titania, zinc oxide and tin oxide. Using the process, we can easily fabricate various shapes of disk and sheet with nanoholes. The disk of oxide nanohole array was able to be prepared up to about 50 μm thickness and 5 cm^2 in diameter. The holes were about 100 nm in diameter and penetrated through the disk. The titania nanohole array as prepared was amorphous and became anatase after annealing at 500C. The titania nanohole array was found to be thermally stable and to be electrochemically active. The oxide nanohole arrays are attractive for a wide variety of application in different fields such as electrical, optical and chemical devices.

P6.12

GROWTH AND SUBSTRATE DEPENDENT ORIENTATION AND BONDING OF 4,4'-BIBENZYL DITHIOL. A.N. Caruso and P.A. Dowben, University of Nebraska, Dept of Physics and Astronomy, Lincoln, NE; R. Rajesekaran and J. Redepinning, University of Nebraska, Dept of Chemistry, Lincoln, NE.

The adsorption of 4,4' by vapor and solution deposition methods results in orthogonal molecular orientations with respect to surface normal. Molecular orientations are determined using symmetry and selection rules for polarization dependent valence band photoemission via synchrotron light. It is evident that self-assembly, final molecular orientation and bond strength of this alkanethiol depend strongly on how thermodynamic equilibrium is achieved during the adsorption process. Many of the molecular orbitals HOMO 9 through LUMO 4 were identified assuming C_{2v} symmetry using combined photoemission and inverse photoemission.

P6.13

LOCALIZED ANODIZATION OF POROUS ALUMINUM OXIDE ON ALUMINUM THIN FILMS. Qiyu Huang and Michael Reed, Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, VA.

Self-assembled porous aluminum oxide formed by the anodic oxidation of bulk aluminum is known to have near vertical sidewalls and controllable pore size, pore spacing and pore densities. It has been widely studied and used in industries as nano-fabrication templates, filters or micro-reactors. But not much study has been done on the localized anodic oxidation of deposited aluminum thin films, which has many potential applications in microelectromechanical systems (MEMS) and biomedical engineering area. In this work, we study the localized anodic oxidation of aluminum thin films. An anodization barrier, comprising a layer of Polymethylmethacrylate (PMMA) or SU-8, is cast onto a 300 nm thick aluminum film, which is evaporated on a silicon wafer with thermally grown silicon dioxide. The barrier is subsequently patterned and the exposed aluminum anodized in a 0.3M oxalic acid solution. Traditional photolithography and nano-indentation of the barrier layer are explored as the patterning techniques. The anodization progress of patterned aluminum thin films is observed and the interface between the anodized region and aluminum region is studied. Different sizes of patterned aluminum dots, ranging from 1 μm to 25 μm , are anodized and the interfaces are compared. A tentative explanation is given on the difference between the interfaces of different size patterns. Extension of this study to smaller dimension patterns is presented. Potential applications and challenges will be discussed.

P6.14

SELF-ASSEMBLY OF SURFACTANTS AT AIR/ORGANIC SALTS. Yongsoo Shin, Glen E. Fryxell, Li-Qiong Wang, and Gerg J. Exarhos, Pacific Northwest National Laboratory, Richland, WA.

Self-assembly of amphiphilic organic molecules into an ordered nanostructure has increasing attention in catalysis, sensing, and biomimetics. Specially utilization of surfactants with long alkyl chains

or block co-polymers have opened a wide range of scientific interests such as biomedical delivery and increased catalytic activities of biomolecules. Many fundamental studies have recently focused on the synthesis of nanostructured organic-inorganic hybrid thin film using alkyltrimethylammonium salts. Such layered silica-surfactant nanocomposites were formed by polymerization of tetraalkoxysilane in aqueous solutions of surfactants. In this paper, we report a self-assembly of amphiphilic molecules on hygroscopic quaternary ammonium salts such as tetrabutylammonium acetate (TBAAc), tetrabutylammonium bromide (TBAB), and tetrabutylammonium nitrate (TBAN) through slow contact to air, where they show different hygroscopicity, $\text{TBAAc} > \text{TBAB} \geq \text{TBAN}$. Homogeneously dissolved surfactants rearrange themselves when they contact air due to high moisture adsorption behavior of such salts. Highly ordered lamellar phases with different lattice spacings have been observed when surfactants with long alkyl chains were used. Surfactant molecules used in this study showed different self-organization based on the property of head groups. Alkylammonium halides forms monolayers, while neutral alkylamines forms bilayers upon basal spacings on X-ray diffraction patterns. A lamellar d spacing observed is closely related to the alkyl lengths of surfactants used in this study. Such materials can be applied for synthesis of ordered metal oxide materials, which are very useful in catalysis, separation technology, and sensors. Intensive XRD, NMR, and microscopic studies will be discussed in detail.

P6.15

ASSEMBLY OF ORIENTED 2-D PROTEIN AND VIRUS ARRAYS. Chin Li Cheung, Julio A. Camarero, Bruce W. Woods, Brandon L. Weeks, Alex Noy, and Jim J. De Yoreo, Lawrence Livermore National Laboratory, Div of Chemistry and Materials Science, Livermore, CA; Tianwei Lin and John E. Johnson, The Scripps Research Institute, Dept of Molecular Biology, La Jolla, CA.

A general approach for the fabrication of oriented 2-dimensional protein and virus arrays has great potential to facilitate the determination of their structure by x-ray diffraction and measurements of their surface potentials. We present here our effort towards the creation of nanoscale ordered templates with site-specific chemical linkers to proteins and viruses by dip-pen nanolithography (DPN). The orientations of these proteins and viruses can be controlled by introducing chemoselective functional groups on their surfaces complementary to the specific chemical linkers on the surface templates. We will present a rapid and efficient solid phase synthesis approach for the preparation of these chemoselective linkers. We will also report results of patterning viruses on templates fabricated by DPN and micro-contact printing. Preliminary results using these templates to direct the growth of virus crystals will also be discussed.

P6.16

NANOCOMPOSITE CATHODES FOR SOLID-STATE LITHIUM BATTERIES. Elsa Olivetti, Anne M. Mayes, Donald R. Sadoway, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

By utilizing the self-organizing character of amphiphilic graft copolymer systems and incorporating continuous nanoscale components, we investigate the fabrication of high energy density cathode materials for solid-state rechargeable batteries. The in-situ growth of inorganic active phases in ion-conducting domains of copolymer systems allows for control of morphology and increases the interface-to-volume ratio, thereby increasing the area over which ion and electron transport can occur. In graft copolymer systems under certain conditions, thermodynamic driving forces induce local segregation or microphase separation of the dissimilar constituents (the backbone and the side chains) into nanoscale periodic domains. Free-radically synthesized poly(oxyethylene) methacrylate-g-poly(dimethyl siloxane), POEM-g-PDMS, with a domain periodicity of 23nm, serves as a structure-directing molecule for the incorporation of active components. Using a sol-gel preparation technique involving ion-exchange protonation of a sodium metavanadate solution, vanadium oxide was incorporated into the swollen copolymer. X-ray diffraction was used to verify the existence of the inorganic component and the microphase separation of the copolymer. The polymer was cryomicrotomed and analyzed with transmission electron microscopy (TEM). Data from dissolution studies suggest that the transition metal sol-gel products incorporate into the hydrophilic domain. The nanoscale structure directing property of the graft copolymer system can also be used to address electronic conductivity in the cathode material. Through techniques such as electroless deposition, metal ions can be chemically reduced followed by further deposition of metal onto the reduced surface.

P6.17

NANOSTRUCTURE OF LIQUID CRYSTALLINE POLY(BENZYL L-GLUTAMATE) - X DIBLOCK COPOLYMER CAST FILMS. Elizabeth Minich and Darrin Pochan, University of Delaware, Newark,

DE; Andrew Nowak and Timothy Deming, University of California at Santa Barbara, Santa Barbara, CA.

Poly(benzyl L-glutamate) (PBLG) forms a rigid helical rod in organic solvents. Cholesteric liquid crystalline ordering of these rods has been observed in PBLG solutions and cast films. In this research, two series of block copolymers were created with PBLG in an attempt to alter the classic PBLG cholesteric phase behavior. First, peptide blocks with inherent secondary structures, random coil or rigid rod, were attached to PBLG molecules. The phase behavior was controlled by altering the block's secondary structure and length relative to the PBLG block. Second, a series of hybrid block copolymers with synthetic polymers of polystyrene and polybutadiene were synthesized. The liquid crystalline/self-assembly ordering of these two molecule series in organic solvent was probed with transmission electron microscopy (TEM), polarizing optical microscopy (POM), and small-angle x-ray scattering (SAXS). In pure PBLG and PBLG blocks with relatively small additional blocks, cholesteric liquid crystalline ordering was observed. However, when the relative block size of the coil block was increased significant changes in the phase behavior was observed. This control over molecular self-assembly and phase behavior reveals the ability to pattern materials with peptidic functionalities by taking advantage of molecular architecture and polymer secondary structure.

P6.18
POLYMERIC ONE-DIMENSIONAL REFLECTORS BASED ON SELF-ORGANIZATION OF COMB-SHAPED SUPRAMOLECULES. Harri Kosonen, Sami Valkama, Janne Ruokolainen, Olli Ikkala, Helsinki Univ of Technology, Dept of Engineering Physics and Mathematics and Center for New Materials, Espoo, FINLAND; Mika Torkkeli and Ritva Serimaa, Univ of Helsinki, Dept of Physics, Helsinki, FINLAND; Gerrit ten Brinke, Univ of Groningen, Lab of Polymer Chemistry and Materials Science Center, Groningen, THE NETHERLANDS.

There has been considerable interest over the recent years to develop periodic dielectric structures to manipulate the flow of light. Such photonic crystals have turned out to be surprisingly difficult to construct using traditional lithographic and etching techniques due to the small structures. On the other hand, spontaneous assemblies allow small enough structures based on colloids, synthetic and inverted opals, and block copolymers. However, in such cases, it is nontrivial to achieve perfectly ordered structure over the macroscopic length scale, which, in addition should contain carefully engineered defects for light channels. Therefore, it may turn out that self-assembly leads to additional, more robust applications where complete photonic bandgap and detailed engineering of defects are not required, still requiring strong interaction with light at given frequencies. We demonstrate that complexation of dodecylbenzenesulphonic acid, DBSA, to a diblock copolymer of polystyrene-*block*-poly(4-vinylpyridine), PS-*block*-P4VP, leads to polymeric supramolecules PS-*block*-P4VP(DBSA)_y for y = 1.0, 1.5, 2.0, which self-organize with a particularly large lamellar periodicity in excess of 1000 /Å. The structures consist of alternating PS and P4VP(DBSA)_y layers, where the latter contains smaller internal structure, probably lamellar. The DBSA side chains are bonded to the pyridines by protonation or hydrogen bonding and they effectively plasticize the material. In this way relatively well-developed structures are obtained even without annealing or macroscopic alignment. Optical measurements show that act as an one-dimensional reflecting mirrors having a photonic bandgap at ca. 420 nm.

P6.19
NOVEL WAYS TO GIVE PORE SIZE VARIATION IN NANO-POROUS STRUCTURES RANGING FROM A FEW NANOMETERS TO TENS OF NANOMETERS BY USING BLOCK COPOLYMERS. Unyong Jeong, Du Yeol Ryu, Jin Kon Kim, Pohang Univ. of Science and Technology, Dept of Chemical Engineering, Pohang, KOREA; Thomas P. Russell, Polymer Science and Engineering Department, Univ. of Massachusetts, Amherst, MA.

Block copolymers which self-assemble to make periodic structures with well-defined size and spacing on the tens of nanometers length scale have attracted a lot of attention due to potential usage as functional nanostructures. The structures are determined by the molecular weight, chemical structure, molecular architecture, and block length ratio of the block copolymers. The controllability of the microdomain sizes as well as the orientation is utmost necessary for application purpose. However, the range of microdomains size and lateral distance between microdomains are simply determined by molecular weight and volume fraction for a given block copolymer. In this study, we suggest novel routes by which the size scale of nanostructures can be extended beyond the bounds achievable with the block copolymers alone. One is to use block copolymer and homopolymer mixture, and the other is to crosslink the matrix by ozone exposure. Polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block

copolymer thin film was prepared to vertically orient PMMA cylindrical nanodomains to the substrate. Diameter of the generated manholes ranges from a few nanometers to tens of nanometers with good ordering regularity. These nanoholes have potential uses to make quantum dots array, nano post with high aspect ratio, bio-material separation media, and storage media without interference.

P6.20
SYNTHESIS OF PHENOL/FURFURAL POLYMER NANOTUBES. Masafumi Uota^a, Daisuke Fujikawa^a, Shinji Mouri^a, Masako Kuroki, Katsuya Kaikake, Mitsunori Yada, Masato Machida^a and Tsuyoshi Kijima^a. ^aDepartment of Applied Chemistry and Department of Applied Physics, Faculty of Engineering, Miyazaki University, Miyazaki, JAPAN, and Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga, JAPAN.

In contrast to carbon-based and other inorganic nanotubular compounds, the organic free nanotubular materials so far reported are classified into either under one-nanometer tubes or over ten-nanometers ones according to the size of their inner diameters. Here we report the first synthesis of phenol-furfural polymer nanotubes of 2-3nm hollow diameters. In the typical fabrication process, phenol and furfural were moderately reacted into cooligomers in the presence of NaOH at 80°C. After the phenolic groups in the cooligomeric species being anionized with a concentrated aqueous solution of NaOH, the resulting solution was added drop wise to a mixed solution of phenol, alkyl trimethyl ammonium bromide (CnTAB; n=8, 12, 16) and water with stirring at temperatures 40-80°C and then kept for 6h. Nanotubular polymers of ca.6nm outer diameter and black in color were obtained as the major phase for the 80°C product. The nanotubular particles formed at temperatures as high as 80°C or above were also observed to be finely dispersed. The inner diameter of the nanotubes ranged from 2 to 3 nm depending on the chain length of the surfactant used. The surfactant incorporated in the as grown nanotube significantly decreased in content with an increase in the reaction temperature. The reaction using cetylamine in place of cationic surfactant as a template yielded surfactant free hollow nanotubes. This is probably because the protonated alkylamine species electrostatically bound to phenoxy groups readily revert to their neutral form, leading to their complete release from the polymer framework.

P6.21
COMPUTER SIMULATION OF SELF-ASSEMBLING NANOSCALE RODS AND SPHERES IN DIBLOCK COPOLYMERS. Mary H. Cheng, Gavin A. Buxton, and Anna C. Balazs, Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA.

Simulations show that mixtures of nanoscale rods and spheres can self-assemble into a rich variety of structures when these particles are blended with AB diblock copolymers. Both types of particles are preferentially wetted by the A blocks and thus, are confined within the A domains of the copolymers. When localized in these A domains, the rods tend to align due to the presence of the spherical particles. Furthermore, both the spheres and rods experience complex repulsive interactions with the soft walls of the domains. Through a variation of the wetting interactions, particle volume fractions and the domain size of the diblocks, we observe a broad range of self-assembled, ordered nanostructures.

P6.22
PREPARATION OF PBS NANO PARTICLES BY CHEMICAL METHODS. T.K. Chaudhuri, N. Saha, J. Vaculic and P. Saha, Polymer Centre Faculty of Technology, Tomas Bata University Zlin, Zlin, CZECH REPUBLIC.

Nano particles of PbS have great potential for photonics since it has a large effective Bohr radius (18 nm) arising from high dielectric constant (17.3) and small effective electron mass. The studies on PbS nano particles has been less as compared to CdS and CdSe as suitable preparation techniques are not available. This paper reports the preparation of PbS nano particles by simple chemical methods. It also reports a new inhibitor for PbS nano particles made from solution. In the first (wet) method methanolic solution of Pb(Ac)2 and thiourea (LAT) was used under different conditions. When a solution was kept at about 25°C, the colour changed gradually from pinkish brown to light brown in 15 min. After 4 h red brown particles were dispersed in the solution which turned black after another 2 h. X-ray diffraction confirmed the formation of PbS. Scanning electron microscope revealed that the particles had flake type structure which coalesced to form spheres. The LAT solution was subjected to ultrasonic waves. The conversion to PbS was faster but the colour of particles in solution changed gradually from yellow, orange, light brown, dark brown and black depending on time. To stop the growth of particle at any stage a new inhibitor, protein hydrolysate, was used by adding its

powder to the solution. Using this inhibitor, solutions of different colours were made. For the dry method of preparation, the methanolic LAT solution was dried and the solid material was pulverised. The white powder obtained was heated in air at 75°C for different duration of time from 5 to 20 mins. The colour of the powder changed from pink to light brown. The nano particles has been characterized by X-ray diffraction and scanning electron microscope.

P6.23

POLYDIACETYLENE BASED NANOCOMPOSITES WITH REVERSIBLE MESOSCOPIC ORDER. Byron McCaughey, Xuan Li, Jiebin Pang, Xiang-Ling Ji, and Yunfeng Lu, Tulane Univ, Chemical Engineering Dept, New Orleans, LA.

Polydiacetylene (PDA) has been the subject of extensive work because of its ability to form stable, ordered thin films that change color due to thermal, mechanical, or chemical stimuli. PDA based nanocomposite thin films have been self-assembled as a result of non-covalent interactions such as hydrogen bonding, pi-pi stacking, hydrophobic, and electrostatic interactions. FTIR, XRD, TEM, AFM, and UV-vis demonstrate nanocomposite formation and provide structural information. Substantial structural and chromic blue-to-red reversibility to thermal stimuli is shown with UV-vis and XRD peak shifts. This reversibility is due to the intramolecular interactions that return PDA side chains to original positions after thermal stress is removed. Reactants with different structures and functionalities were used to study changes on composite properties and provide a fundamental understanding of the thermochromic mechanism in this system.

P6.24

SELF-ASSEMBLED, INTERCALATED, RESPONSIVE POLYDIACETYLENE BASED CRYSTALS. Xuan Li, Byron McCaughey, Jiebin Pang, Xiang-Ling Ji, and Yunfeng Lu, Tulane Univ, Chemical Eng Dept, New Orleans, LA.

Organic crystals have attracted a great deal of attention because final material properties and applicability may depend on the original crystal structure and the synthesis method utilized. Polydiacetylene (PDA) has been the subject of extensive work because of its ability to form stable, ordered crystals that change color due to thermal, mechanical, or chemical stimuli. In this research, PDA based nanocomposite crystals with various mesostructures (e.g. hexagonal, lamellar, and cubic) containing removable functional organic moieties have been synthesized based on non-covalent interactions such as hydrogen bonding, pi-pi stacking, hydrophobic, and electrostatic interactions. The organic moieties can be reversibly intercalated within the reacted, mesostructured PDA crystals. A variety of crystals with different mesostructures were synthesized using different organic moieties and PDA precursors. XRD, TEM, AFM, and UV-vis have been used to characterize the nanocomposite crystal structure and responsiveness to the intercalation process.

P6.25

IONIC GROUP EFFECT ON THE MICELLIZATION OF RANDOM IONOMER IN DMF/WATER MIXED SOLVENT. Sung-Hwa Oh, Department of Polymer Science & Engineering, Chosun University, Gwangju, KOREA; Jeong-a Yu, Department of Science Education, Chosun University, Gwangju, KOREA.

Micelle formation requires two opposing forces. An attractive force between the amphiphilic molecules leading to aggregation and the opposing force that prevents the unlimited growth of the micelle. Among factors, the polarity of solvent and the content of ionic units play an important role for morphology of ionomers in solution. Depending on the polarity of solvent, ionomers show either polyelectrolyte behavior [in polar solvent such as dimethylformamide(DMF)] or aggregation behavior[in non-polar solvent such as tetrahydrofuran(THF)]. As a hydrophobic repeat unit, styrene is a well-known model compound for the studies of random ionomers. However, there are only a few of the studies on the behavior of polystyrene based ionomers in water because hydrophobic polystyrene is not soluble in water. In the present study, we have shown that poly(styrene-co-sodium methacrylate) [P(S-co-MANa)] with various contents of ionic repeat units can form transparent colloidal aggregates if an ionomer in DMF, a good solvent for styrene and methacrylate units, is added to an excess amount of water in drop-wise manner. Molar ratio of DMF to water was kept at 1/450 (~1v%). Critical micelle (or aggregates) concentrations (CMCs) and the size distributions of micelles formed from P(S-co-MANa) in DMF/water solutions were obtained by spectroscopic methods and light scattering technique, respectively. The fluorescence and the uv-visible spectroscopic measurements were utilized with pyrene as a probe molecule. The measurements were made for P(S-co-MANa) with mol % of methacrylate in the range of 3.66-9.24 mol%. As the content of ionic unit increased, CMCs of ionomers increased slightly and the obtained CMCs were in the range of $1.4\sim 2.8 \times 10^{-6}$ g/mL at

room temperature. The size of the formed micelle was in the range of 20-30 nm. For comparison, we also measured CMC and the size of micelle formed from polystyrene homopolymer and were 1.0×10^{-6} g/mL and $\sim 1\mu\text{m}$, respectively.

P6.26

HEXAGONALLY PACKED CYLINDERS OF DIBLOCK COPOLYMERS. STRUCTURE AND RHEOLOGICAL BEHAVIOR OF THE DISPERSED PHASE IN WATER. Julien Grandjean, Ahmed Mourchid, CNRS-Rhodia, Complex Fluids Lab., Cranbury, NJ.

Amphiphilic diblock copolymers have shown the ability to form organized structures with different shapes like spheres, cylinders and lamellae. These morphologies are mainly controlled by the chemical incompatibility between the two blocks, their relative volume and the method of dispersion. We study aqueous suspensions of hexagonally packed cylinders of polystyrene-poly(acrylic acid) copolymers. The core is made of glassy polystyrene, which keeps the structure frozen upon dilution. We present results on the swelling behavior, the rheology and the structure under shear of these systems. At high polymer concentration, the swollen structure is compact and exhibits a solid-like behavior with very high viscoelastic moduli. At intermediate polymer concentration range the swelling departs from the dilution law of cylinders. In this concentration domain the excess of water triggers a microscopic phase separation. The elasticity of the gels then decreases dramatically upon further dilution. Below 1.5 wt. %, a gel-to-liquid transition, with a macroscopic phase separation, occurs. We will discuss these features taking into account the stretching of the polyelectrolyte brushes and its evolution with the osmotic pressure of added salt. Finally, neutron scattering experiments under shear raise challenging questions in contrast with the flow behavior usually observed for cylindrical particles. Instead of the expected alignment of 1D objects, structure study under shear revealed an orientation of the cylinders in the direction of the shear gradient. This behavior suggests that the cylinders are packed in 2D layers. The effect of flow consists in the alignment of these microdomains. This picture is compatible with the results of the swelling behavior pointed out before.

P6.27

TEMPERATURE DEPENDENCE OF THE SELF-ASSEMBLED STYRENE BASED RANDOM IONOMERS IN AQUEOUS SOLUTION. Sung-Hwa Oh, Department of Polymer Science & Engineering, Chosun University, Gwangju, KOREA; Hyang-Rim Oh, Department of Science Education, Chosun University, Gwangju, KOREA; Mu Seong Kim, Department of Polymer Science & Engineering, Chosun University, Gwangju, KOREA; Ju-Myung Song, Department of Polymer Science & Engineering, Chosun University, Gwangju, KOREA; Joon-Seop Kim, Department of Polymer Science & Engineering, Chosun University, Gwangju, KOREA; Jeong-a Yu, Department of Science Education, Chosun University, Gwangju, KOREA.

Over two decades, the properties and morphology of self-assembled ionomers in polar and non-polar solvents have been studied extensively. Depending on the composition of copolymer and the properties of solvent, ionomers can form micelles showing multiple morphologies, which thermodynamically favor one of the amphiphilic repeat units. Three types of ionomers in solution have been studied widely: block ionomers, telechelic ionomers, and random ionomers. However, most studies were performed on the block ionomers, and only few studies on the structures of random ionomers in solution were published. Many investigations performed on block ionomers indicate that temperature as well as the copolymer structure and solvent polarity markedly influences the free chain-micelle equilibrium and the micelle structure. In this study, to understand the temperature effect on the self-assembly behavior of random ionomers, we prepared nano-sized micelle from Poly(styrene-co-sodium methacrylate) [P(S-co-MANa)] in water containing trace of dimethylformamide(DMF); molar ratio of DMF/water was kept at 1/450 (~1v%). The molar ratios of methacrylate unit to water-insoluble styrene were in the range of 0.036-0.09. The temperature dependence of critical micelle concentrations (CMCs) was obtained by using an uv-visible and the fluorescence spectroscopic techniques utilized with pyrene as a probe molecule. The CMCs measurements of ionomers with various contents of ionic units were performed in temperature range of 10-80°C. As the temperature increased from 10°C to 80°C, the CMCs increased one order of magnitude, from 10^{-6} to 10^{-5} g/mL. A Plot of logarithmic CMC as a function of (absolute temperature)⁻¹ showed linear behaviors with two different slopes. One showed negative values of slope (ΔH) and intersect (ΔS), and the other had a negative slope and a positive intersect indicating the environment of pyrene, a probe molecule, changed twice as the temperature increased. In this presentation, we will discuss the details of the observed results.

P6.28

FIBROUS SELF-ASSEMBLY OF LOW-MOLECULAR-WEIGHT GELATORS: MORPHOLOGIES AND FUNCTIONS CONTROLLED BY HYDROGEN BONDS. Kazuhiro Yabuuchi, Emmanuel Marfo-Owusu, Takashi Kato, The Univ of Tokyo, Dept of Chemistry and Biotechnology, School of Engineering, Tokyo, JAPAN.

There are growing interests in self-assembled fibers of low-molecular-weight compounds because of their morphological features and potential for nanostructured functional materials. Fibrous molecular self-assembly on the nanometer-scale occurs in various organic solvents through noncovalent intermolecular interactions, mainly, hydrogen bonding. Formation of three-dimensional network of these self-assembled fibers often leads to the physical gelation of the solvent. For the design of such materials, the control of hydrogen bonds is of great importance. Hydrogen-bonded structures exert great effects on various properties of fibers and gels. We have studied self-assembly behavior of some low-molecular-weight gelators in common organic solvents and liquid crystals. Gelators with a benzene core and two urea moieties formed thick aggregates in solvents, resulting in poor gelation ability because the urea moieties were involved in bifurcated hydrogen bonding which formed stable hydrogen-bonded one-dimensional arrays. Introduction of pyridyl moiety to urea gelators had favorable effects on gelation ability due to the change of fiber morphology. Moreover, when liquid crystals were gelled by the pyridine gelator, good electrooptic effects of liquid-crystalline gels were achieved. This was due to the formation of a finely-dispersed network of elongated fibers. X-ray crystallography revealed that the pyridine gelator formed a unique hydrogen-bonding pattern. The pyridyl nitrogen acted as a hydrogen bond acceptor, which partially disturbed the formation of bifurcated hydrogen bonds between urea units. Intramolecular hydrogen bonds were formed instead between pyridyl nitrogen and one of two urea units. The other urea unit formed bifurcated hydrogen bonds. Thus, the formation of intramolecular hydrogen bonds plays a key role for the self-assembly of elongated fibers in solvents. The results indicate that the pyridine-based bisurea gelator is a good gelator not only in terms of its effectiveness of gelation ability but also as a component of functional soft materials.

P6.29

BIOINSPIRED NANOCOMPOSITES. Yahik Krikorian, Darrin J. Pochan, Univ of Delaware, Dept of Materials Science and Engineering and Delaware Biotechnology Institute, Newark, DE; Andrew P. Nowak, Timothy J. Deming, Dept of Materials, Univ of California Santa Barbara, CA.

In this investigation the possibility of making rigid polymer layered nanocomposites from biocompatible/biodegradable matrices was explored. Three types of commercially available organophilic clays were employed in order to concurrently study the effect of hydrophobicity of the surfactant on the overall nanocomposite formation. The nanocomposites were fabricated via the exfoliation adsorption technique using Poly(L-lactic acid), PLLA, a widely used biodegradable synthetic polyester, as the polymeric matrix. Wide Angle X-ray Scattering (WAXS) data reveals that decreasing the hydrophobicity of the surfactant increases the tendency of the system to exfoliate and randomly distribute the silicate layers throughout the matrix. Transmission electron microscopy (TEM) data shows the ordering of silicate platelets is consistent with the d-spacings obtained from WAXS. Due to the nanometer range dispersion of silicate layers all the nanocomposites retain their optical clarity. Mechanical properties of the fabricated nanocomposites were probed by dynamic mechanical analysis and tensile testing techniques and show significant improvements both in terms of toughness and stiffness when compared to neat PLLA. In order to show the potential application of these systems in biological environments, results of mammalian cell culturing experiments will also be discussed.

P6.30

ION MEDIATED TUNING OF THE SURFACE HYDROPHOBICITY IN THIN FILMS OF OLIGOETHER FUNCTIONALIZED POLY(P-PHENYLENE) BASED MIXED IONIC ELECTRONIC CONDUCTORS. F.P. Wenzl, Technische Universitaet Graz, Inst. f. Festkoerperphysik, AUSTRIA; C. Stuess, Joanneum Research GmbH, Inst. f. Nanostrukturierte Materialien und Photonik, Weiz, AUSTRIA; E.J.W. List, Christian Doppler Laboratory for Advanced Functional Materials, Technische Universitaet Graz, Inst. f. Festkoerperphysik, AUSTRIA; Joanneum Research GmbH, Inst. f. Nanostrukturierte Materialien und Photonik, Weiz, AUSTRIA; M. Bouguettaya and J.R. Reynolds, Center for Macromolecular Science and Engineering, University of Florida, FL; G. Leising, Science and Technology, AT&S AG, Leoben, AUSTRIA, and Joanneum Research GmbH, Inst. f. Nanostrukturierte Materialien und Photonik, Weiz, AUSTRIA.

We report on quantitative x-ray photoelectron spectroscopy (XPS)

studies on the surface composition of a polymeric mixed ionic electronic conductor (PMIEC). The polymer consists of a hydrophobic conjugated poly(p-phenylene) (PPP) backbone functionalized with hydrophilic oligo(ethylene oxide) (OEO) side-chains. The carbon:oxygen ratio at the surface of a thin film of the pristine polymer corresponds to its chemical composition, indicating that the upper surface is homogeneously composed of both polymer backbones and side-chains. The surface carbon:oxygen ratio strongly decreases after the addition of low amounts of a Li salt (lithium triflate, LiTf), but returns to near the value of the pristine film at higher salt concentrations for which infrared spectroscopic studies have revealed enhanced ion aggregation. This behavior is similar to that for pristine OEO:LiTf complexes where, at low salt concentrations, a reduction of the surface tension is caused by the presence of dissociated ionic species at the surface, but at higher salt concentrations the surface tension increases due to an enhanced tendency for ion aggregation. One can therefore tune the surface composition, and thereby the surface hydrophobicity of PMIECs, by the amount and the ion association tendency of a specific salt added.

P6.31

NOVEL MATERIALS BASED ON ORGANIC-TUNGSTEN OXIDE HYBRID SYSTEMS. B. Ingham, Victoria University of Wellington, Wellington, NEW ZEALAND; S.V. Chong and J.L. Tallon, Industrial Research Limited, Lower Hutt, NEW ZEALAND.

Tungsten trioxide, and its related compounds, has been the subject of research for many years. One of its well-known structural forms is that of the cubic tungsten bronzes, where alkali metals such as sodium or potassium are doped into the vacant Perovskite "B"-site between the WO₆ octahedra. More recently, our research has focused on the separation of tungsten oxide layers by organic spacer molecules such as diaminoalkanes, benzylamine and phenethylamine. Diaminoalkane tungsten oxides were synthesised by reacting stoichiometric amounts of diaminoalkane with tungstic acid (H₂WO₄) in ammonia solution. The d-spacing of these hybrids as given by powder X-ray diffraction (XRD) indicates that the lattice expansion with increasing alkane number agrees with first principle calculations of the cell-length, based on a single layer of tungsten oxide with the diaminoalkanes aligned perpendicular to the inorganic layer. The electronic properties of the new hybrid materials were examined by UV-visible spectroscopy and photoluminescence, and compared with the same for bare WO₃. The UV-visible spectra indicate an increase in the band-gap energy; the amount of which depends on the organic spacer molecule incorporated. Preliminary results of photoluminescence measurements appear to show broad emission peaks in the visible region. Field-effect devices have been fabricated and tested for spin-coated WO₃ films. *Abinitio* computational methods have also been utilised to explore the nature of WO₃-based materials. This work has initially focused on the electronic and physical crystal structures of the tungsten bronzes with intercalated Group I atoms, but will be extended to the organic-inorganic hybrid materials. The relaxation of the cubic Na_xWO₃ system resulted in a linear relationship of cell size versus x. The band structure around the Fermi level has also been calculated for this system which again shows a systematic trend as a function of Na doping, with a metal-insulator transition at low doping values.

P6.32

SPIN-COATING SELF-ASSEMBLY FOR MICROPATTERNING OF ULTRATHIN MULTILAYER FILMS. Hongseok Jang, Sangcheol Kim, and Kookheon Char, Seoul National University, School of Chemical Engineering, Seoul, KOREA.

A new approach to create ultrathin multilayer films with well-defined micropatterns in short process time is introduced. To achieve such micropatterns with high line resolution in organic multilayer films, microfluidic channels were combined with the convective self-assembly process employing both hydrogen bonding and electrostatic intermolecular interactions. The channels were initially filled with polymer solution by the capillary pressure and the residual solution was then removed by the spinning process. During these repeated two steps, the polymers were allowed to adsorb onto the surface. For alternating poly(4-vinylpyridine) (PVP) and poly(acrylic acid) (PAA) multilayers, the micropatterns with sharp line boundaries were obtained and the small ridges at the edges of the patterned lines were also observed. The resulting patterns were then used as templates for the fabrication of multilayer micropatterns with vertical heterostructure. The spin-coating self-assembly process of poly(diallyldimethyl ammonium chloride) (PDAC) and poly(sodium 4-styrenesulfonate) (PSS) was performed on the micropatterned (PVP/PAA)₅ template. The internally heterostructural micropatterns with sharp edge boundaries were obtained for (PVP/PAA)₅/(PDAC/PSS)₄₀ composite multilayers.

P6.33

SELF-ASSEMBLED ORGANIC-INORGANIC SILICA HYBRIDS FROM POLYVIIOLOGENS. G.M. Gray, J.N. Hay, Chemistry,

University of Surrey, Guildford, Surrey, UNITED KINGDOM.

Polyviologens (bipyridinium polymers) can be synthesized by the Menshutkin reaction and incorporated into silica hybrids using the hydrolytic sol-gel route. Transparent sol-gel hybrids can be obtained with up to 75% polyviologen content, indicating a likely nanoscale morphology. Nitrogen adsorption-desorption studies show that the hybrids are mostly mesoporous solids, but porosities are very low at high polymer contents. The polyviologens are believed to act as non-bonding templates, controlling the growth of the silica network through electrostatic interactions between the quaternary nitrogen atoms of the polymer and the silanol oxygen atoms in the silica network. The effectiveness of amino acids and peptides towards silicic acid polymerisation has also been attributed to similar electrostatic and hydrogen bond interactions. Our investigations with polyviologens have revealed them to be effective catalysts for silicic acid polymerisation under mild conditions.

P6.34

SELF-ASSEMBLED PS-PMMA BLENDS PREPARED BY SPIN-CASTING. Glaura Goulart Silva, Patricia Mara de Freitas Rocha, Patricia Santiago de Oliveira, Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL; Bernardo Ruegger Almeida Neves, Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL.

Polystyrene/poly(methylmethacrylate) blends (PS/PMMA) are completely phase-separated materials and remain so at elevated temperatures. Domain sizes of these amorphous blends are dependent of various factors such as molecular weight of the polymers, preparation method of the blend and composition. In this work, blends PS/PMMA with 40:60 and 60:40 wt% ratio were prepared with two different PS, showing glass transitions (T_g) at 100°C and 60°C. PMMA of $T_g = 120^\circ\text{C}$ was mixed with PS using three different methods: melting mixing, casting from solution and spin-casting. The thermal properties of the blends were studied by using modulated differential scanning calorimetry (MTDSC) which enhances the ability to detect glass transitions of phase separated materials in relation to conventional DSC. Insights into the size, shape and distribution of phases were obtained by atomic force microscopy (AFM) using intermittent contact mode. The AFM topographic and phase contrast images indicated that the melting mixing blends have domain sizes larger than the micron and the casting materials are submicron phase separated. The images obtained for the spin-casting blends showed that this method of preparation allowed the self-assembling of the different phases in an organized pattern. The images also indicated the presence of two scales of domain sizes: a submicron phase separated and a nanometric one. The influence of different morphologies into glass transition results is discussed. The fact that AFM probes blend surfaces and that MTDSC is a bulk measurement is taken into account.

P6.35

MICROPHASE ORDERING OF BLOCK COPOLYMERS CONTAINING COATED PARTICLES. Jae Youn Lee, Russell B. Thompson^a, Anna C. Balazs, Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA; Randall M. Hill, Dow Corning Corporation, Midland, MI. ^aCurrent address: Los Alamos National Laboratory.

Mixtures of diblock copolymers and nanoscopic particles can self-assemble into a wide range of ordered structures. The outcome of such microphase ordering may depend on the chemical and physical nature of each species. One way to control characteristics of particle additives is to coat the particles with chains of desired chemical properties. We employ a numerical method that combines a self-consistent field theory (SCFT) for polymers and a density functional theory (DFT) for particles to investigate the phase behavior of diblock copolymer/coated particle mixtures. We find that the phase behavior of such mixtures differs significantly from that of pure diblock melts or mixtures that contain uncoated particles. The findings can establish guidelines for tailoring the morphologies of diblock/nanoparticle mixtures by modifying particle properties.

P6.36

LIPOSOME STABILITY VERIFICATION BY ATOMIC FORCE MICROSCOPY. Elizabeth de Souza, PUC-Campinas, Faculdade de Química, Campinas, SP; Omar Teschke, IFGW/UNICAMP, Nano-Structure Laboratory, Campinas, SP, BRAZIL.

The observation of liposomes made up of phospholipides by atomic force microscopy has enabled direct visualization of their structure. Liposome/substrate interaction forces were modified by using various surface treatment processes. The images of liposomes supported on mica in air display multiple and single vesicles and also flat bilayers. Molecularly resolved force versus distance curves of the liposomes supported on silanized mica in water display the organization of

hydrocarbon chains and corroborate the presence of distinct adsorbed structures observed in air. The liposomes respond elastically to small stress but undergo plastic deformation when stresses are severe. The rupture force necessary to perforate the top bilayer of the liposome is ~ 0.1 nN and the one corresponding to the adsorbed bilayer on the mica is ~ 0.35 nN. The rupture force decreases as the bilayers are further a part from the mica substrate. Multiple vesicle liposomes adsorbed on mica and observed within liquids and air show the same average diameter as the ones measured by photon correlation spectroscopy, indicating that their size was unchanged during the drying process. Consequently the as prepared liposomes are already formed by smaller vesicles that aggregate to give the ~ 200 nm diameter vesicles. When the liposome interacts with a charged substrate (like mica) the structure formed by aggregation of various vesicles has a greater stability than the one formed by a single spherical vesicle.

P6.37

THIN FILMS OF DIBLOCK COPOLYMERS AND THEIR MICELLES WITH NANOPARTICLES. B.H. Sohn, S.H. Yun, S.I. Yoo, D.H. Park, S.M. Yoo, J.M. Choi, Y.S. Oh, Dept of Materials Sci & Eng, Polymer Research Institute, Pohang University of Sci & Tech, Pohang, KOREA.

Diblock copolymers composed of two different polymers, covalently linked, spontaneously self-assemble into structures on the tens of nanometer scale, whether in bulk or in a solution. With a symmetric diblock copolymer, for example, multilayers of macroscopically parallel lamellae to the substrate can be generated if the substrate has preferential interaction with one of the block. By utilization of the self-assembled multilayer of diblock copolymers, we will demonstrate a parallel process for fabrication of a multilayered nanostructure of alternating pure polymeric layers and nanoparticle-containing layers, both in a nanometer thickness, without a layer-by-layer process. In a selective solvent for one of the blocks, for another example, diblock copolymers spontaneously self-assemble into nanometer-sized micelles consisting of a soluble corona and an insoluble core above the critical micelle concentration. By simple spin coating from a solution of diblock copolymer micelles, a monolayer film of micelles in a short-range hexagonal order can be fabricated by adjusting the solution concentration and spin rpm. In addition, core-corona inversion of diblock copolymer micelles can be induced in situ in the micellar monolayer film by treatment with a selective solvent for the core without a change of micellar packing. With this convertible monolayer of nanometer-sized diblock copolymer micelles, we will show nanopattern formation of functional materials such as nanoparticles, conducting polymers, and magnetic oxides.

P6.38

SELF-ORGANIZATION OF GOLD NANOPARTICLES ON SURFACE-MODIFIED POLY(3,4-ETHYLENEDI-OXYTHIOPHENE) FILMS. Donghui Zhang, Sarah Klapman, Timothy Hanks, Furman University, Dept of Chemistry, Greenville, SC.

The treatment of conducting polymers, such as PEDOT (poly(3,4-ethylenedioxythiophene)), with long chain thiols leads to "near-monolayer" assemblies on the surface. This profoundly affects the surface properties of the film. Here, we investigate thiols containing the diacetylene functional group near the center of the alkyl chain and discuss how this moiety can be used as a surface anchor for attaching other diacetylene-containing species to the PEDOT surface. In particular, it has been found that the derivatization of the polymer film influences the organization of gold nanoparticles (stabilized by identical long-chain thiols) on the surface. When the thiols on both the PEDOT surface and the nanoparticles contain the diacetylene moiety, interdigitation may lead to a geometry suitable for photopolymerization. The potential application of this concept to photopatterning and multilayer assemblies will be discussed.

P6.39

SELF-ASSEMBLED POLYMER NANOSTRUCTURES AND THEIR TEMPLATED METAL OXIDES. Alex D.Q. Li, Ming Qiang Zhu, and Jason Han.

The general strategy in designing nanostructured materials is to employ macromolecular self-organization or to direct synthesis at the nanoscale using a template. In this report, we will discuss the formation of nanostructures including nanospheres and nano-wire like structures. One of our goals to generate such nanostructures is to incorporate controlled absorb or release properties so that hollow spheres can function as delivery vehicles for organic molecules. We have used a class of enzymatic compounds, cyclodextrins as such candidates because they have hydrophobic cavities suitable for inclusion of many organic molecules. Currently, we employ cyclodextrins and diisocyanates to synthesize a class of polymers with

nanostructured pores. Another goal is to construct polymeric nanostructures and then use such as nanostructures to direct the nanostructured materials formation of inorganic metal oxides, especially those metal oxides that have important technological applications.

SESSION P7: SELF-ASSEMBLED POLYMERIC SYSTEMS I

Thursday Morning, April 24, 2003
Metropolitan III (Argent)

8:30 AM P7.1

ULTRAFAST SPECTROSCOPY OF A SELF-ORGANIZED DISCOTIC LIQUID CRYSTAL FOR PHOTOVOLTAIC APPLICATIONS. Clément Daniel, Lukas Schmidt-Mende, Natalie Stutzmann, Richard H. Friend, Carlos Silva, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM; Mark Watson and Klaus Müllen, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

We report combined femtosecond transient absorption (FTA), quasi-steady-state absorption (CW-PIA) and time-resolved photoluminescence (TRPL) measurements on self-organised discotic liquid crystals (LCs) that have been used successfully in photovoltaic devices. We focus on a discotic LC consisting of hexaphenyl-substituted hexa-peri-hexabenzocoronene (HBC-PhC₁₂). We explore the exciton dynamics of HBC-PhC₁₂ in thin films, in chloroform solution and in stack-aligned films. The combined information allows separation of isolated HBC-PhC₁₂ dynamics and those that result from supramolecular assemblies. Combined FTA and CW-PIA measurements of HBC-PhC₁₂ films show that a broad photoinduced absorption appears at very early times (within 100 fs) after photoexcitation and decays with a distribution of timescales that includes very slow components (in the order of ms). We interpret this transient feature as absorption of metastable states that are populated through ultrafast non-radiative transition from the first optically allowed excited state. The dynamics of these metastable states are distinct from those of the optically active state, as measured with TRPL spectroscopy. Polarized TRPL measurements show that the main PL component decays monoexponentially with a lifetime of 17 ns and a constant polarisation anisotropy close to 0.05. However, the PL at the blue edge displays temperature-dependent multiexponential decay (not present in solution) and positive anisotropy at room temperature but negative anisotropy at low temperatures. We interpret this as an emission from delocalized excited states populated through a transfer from the discotic excited states. The measured anisotropy values depend on the structure of the discotic molecule and on their organization in the solid phase. To investigate the phase effects, we also study similar HBC derivatives with crystalline phases at room temperature. Finally, quantum chemical calculations of the electronic couplings in both phases will give an insight into the nature of electronic transitions in this class of discotic materials.

8:45 AM P7.2

HYDROGEN-BONDED DIMERIZATION OF THE [60]FULLERENE DERIVATIVES: SYNTHESIS AND ASSEMBLY. Yuliang Li, Daoben Zhu, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P.R. CHINA.

Hydrogen bonds are essential for molecular recognition and self-organization of molecules in supramolecular chemistry and have been used for the design of various molecular aggregates in solid state or solution. 2,6-diacylamino pyridine and uracil have been chosen as core components to obtain supramolecular systems linked through triple hydrogen bonding. Here a novel supramolecular C₆₀-dimer connected through a three-point hydrogen-bonding interaction of two azafullerene derivatives containing 2,6-diacylaminopyridine and uracil unit respectively has been synthesized. The SEM image shows that the nanoparticles size distribution is rather narrow and exhibited the features of a log-normal distribution.

9:00 AM *P7.3

FABRICATING ORDERED POLYMER MICROSTRUCTURES BY USING LIQUID TEMPLATES. Jiacong Shen, Bai Yang, and Guang Lu, Key Lab of Supramolecular Structure & Materials, College of Chemistry, Jilin University, Changchun, P.R. CHINA.

Polymeric materials with ordered microstructures are of great importance to a range of areas such as the fabrication of optical devices, electronic devices, actuators, sensors, and even polymer-based circuits. Most current techniques, for example, conventional lithography, extreme ultraviolet lithography, soft lithography, embossing, cold-welding, use metallic, semiconductor, or polymeric masks or molds to transfer relief structures into polymeric materials. Recently, using some techniques such as conventional lithography, microcontact printing (CP), and vapor deposition, various solid

surfaces can be patterned into micrometer-sized areas with different wettabilities. These patterned surfaces can be used to direct the condensation of water and self-organization of organic liquids for forming ordered microstructures of liquids. We report that these resulting ordered microstructures of liquids could be subsequently used as templates to fabricate ordered two-dimensional arrays of polymer rings with submicrometer-sized features by combining with a surface-directed and solution concentration-controlled dewetting, porous polymer films with dual scale-ordered microstructures by casting a dilute solution of polymer in a volatile solvent on a water-patterned substrate in the presence of moist air, and ordered voids in a colloidal crystal film-substrate system by combining with the vertical deposition technique.

9:30 AM P7.4

SILVER-POLYIMIDE NANOCOMPOSITE MEMBRANES: SELF-GENERATED HIGHLY REFLECTIVE FLEXIBLE MIRRORED SURFACES. R.E. Southward, Langley Research Center, National Aeronautics and Space Administration, Hampton, VA; M. Pevzner, J.L. Scott, S.T. Broadwater, C.J. Dean, and D.W. Thompson, Dept of Chemistry, William and Mary, Williamsburg, VA.

Surface and bulk silver-metallized polymeric membranes are of interest for solar sail technology, anti-infective medical devices, solar concentrators, thermal blankets, integrated circuitry, gas permeation selective barriers, etc. Here we describe the synthesis of highly reflective flexible polyimide films by a single-stage auto-metallization process involving the {hexafluoroacetylacetonato}silver{I} complex dissolved in solutions of poly(amic acids) and polyimides which are formed from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride (6FDA) and 2,2-bis(4-[4-aminophenoxy]hexafluoropropane {4-BDAF}). Thermal curing of cast silver{I}-poly{amic acid} films leads to cycloimidization with concomitant Ag{I} reduction and nano-aggregation giving a reflective film for Ag concentrations from 2-13 weight percent. A 2% Ag film gives specular reflectivities from 80-90% of vapor deposited Ag. The metallized 6FDA-based films retain the mechanical properties of undoped films and have excellent thermal stability. The bulk of the membrane also contains nanometer-sized Ag particles. TEM and SEM establish that films have surface layers of Ag 30-100 nm thick. In general, films prepared with the silver{I}-hexafluoroacetylacetonate complex are reflective but not conductive, the metallized surface being composed of closely packed nanometer-sized spheres. This is to be contrasted with our earlier work with BTDA/ODA that gave both reflective and conductive films. Films prepared from the soluble fully imidized form of 6FDA/4-BDAF rather than from the amic acid were generally less reflective and more irregular in surface morphology than those prepared from the poly{amic acid}. The metallized films were characterized with respect to conductivity, reflectivity, surface morphology, thermal, chemical, and mechanical properties.

9:45 AM P7.5

EFFECT OF SPHERICAL NANOPARTICLES ON THE SELF-ASSEMBLY OF DIBLOCK COPOLYMERS. Alexander I. Chervanyov and Anna C. Balazs, Pittsburgh Univ., Pittsburgh, PA.

The effect of spherical fillers on the thermodynamic state of a diblock copolymer mixture is investigated. The model mean-field equations are derived to describe the segment number density distribution around a spherical particle. The polymer density profiles are calculated for different types of interaction between polymer segments and particle. Both effects of the incompressibility and Flory-Huggins interaction between segments on the polymer density profiles are taken into account. It is shown that the equilibrium segment density profile around a particle is formed as a result of the competition between the depletion forces and the Flory-Huggins interaction between copolymer segments. Specific examples of the polymer density profiles in the vicinity of a spherical particle are presented. The correction to the free energy of a copolymer system caused by the presence of fillers is found as a sum of the two distinct contributions. The first contribution comes from the depletion interaction between copolymers and particles. The second contribution is due to the reduction of the contact (Flory-Huggins) interaction energy in the vicinity of particles caused by the particle-polymer interaction. It is shown that the competition between the above contributions to the free energy determines the whole effect of fillers on the state of a copolymer system. The magnitude and sign of this effect are found to be strictly dependent on the relationship between the polymer compressibility, segregation factor and the specific character of the polymer-particle interaction. The obtained results make it possible to investigate the effect of spherical fillers on the order-disorder transition of the disordered copolymer system to the lamellae phase. The critical values of the segregation factor χN are calculated from the obtained general expression for the free energy of a filled copolymer system. The dependence of χN on the particle radius and the polymer compressibility factor is studied.

10:30 AM *P7.6

ARRAYS OF MAGNETIC NANOWIRES VIA BLOCK COPOLYMER TEMPLATES. T.P. Russell, Polymer Science and Engineering Department, University of Massachusetts Amherst, Amherst, MA; M.Tuominen, Physics Department, University of Massachusetts Amherst, Amherst, MA.

Arrays of magnetic nanowires and nanowire devices were fabricated using nanoporous templates derived from self-assembling diblock copolymer films. Poly(styrene-methacrylate) (PS-PMMA) diblock copolymers as porous templates that were used to fabricate hexagonal arrays of vertical nanowires with densities of exceeding 1×10^{12} per square inch. Electrodeposition within the template produces 10nm-scale magnetic cobalt nanowire arrays that exhibit large perpendicular coercivity and remanence making them potential candidates for ultrahigh-density perpendicular magnetic storage media. The internal crystal morphology of the nanowires, and consequently magnetic properties, can be manipulated and tuned by electrodeposition process parameters. The copolymer templates have been patterned laterally using conventional lithographic exposure to fabricate novel 3D magnetic nanowire devices. This includes current-in-plane magnetoresistive devices and current-through-wire switching field devices. Anisotropic magnetoresistance measurements show a sharp and complete magnetization reversal, indicating single-domain nanowire switching behavior. Such properties offer promising potential for new magnetic nanodevices built upon on single-domain elements. This work is supported by National Science Foundation Nanoscale Interdisciplinary Research Team, Materials Research Science and Engineering Center and the Department of Energy.

11:00 AM P7.7

SELF-ASSEMBLY OF MESOSTRUCTURED CONJUGATED POLY(2,5-THIENYLENE ETHYNYLENE)/SILICA NANOCOMPOSITES. Byron McCaughey, Tulane Univ, Dept of Chemical Engineering, New Orleans, LA; Chris Costello, Tulane Univ, Dept of Chemistry, New Orleans, LA; Donghai Wang, Eric Hampsey, Tulane Univ, Dept of Chemical Engineering, New Orleans, LA; Chaojun Li, Tulane Univ, Dept of Chemistry, New Orleans, LA; C. Jeffrey Brinker, Sandia National Laboratories, Albuquerque, NM; Yunfeng Lu, Tulane Univ, Dept of Chemical Engineering, New Orleans, LA.

Conjugated polymer-ceramic nanocomposites have been extensively researched because they have shown enhanced conductivity, mechanical strength, processability, environmental stability, and other unique properties. Our research focuses on the synthesis of mesostructured conjugated poly(2,5-thienylene ethynylene) (PTE)/silica nanocomposites. The synthesis approach involves surfactant-induced partitioning, self-assembly and coorganization of 2,5-diiodothiophene monomer and palladium-based catalyst within a poly silicic acid matrix. Subsequent living polymerization initiated by exposing the monomer/catalyst/silica nanostructures to acetylene gas resulted in the formation of an ordered, mesostructured poly(2,5-thienylene ethynylene)/silica nanocomposite as determined by UV-vis, FTIR, XRD, and TEM experiments. PTE formation was verified by a broad UV adsorption between 300 and 600 nm that changed position based on catalyst and monomer concentration. XRD scans and TEM images demonstrate that a cubic PTE/silica mesostructure has been formed. PTE incorporation within the mesoporous silica was determined by an increase in XRD d-spacing on a series of spin-coated samples containing silica, surfactant, and: no monomer or catalyst; monomer and catalyst, and polymer and catalyst (e.g. the [210] peak shifts from 49 to 52 Å respectively). Also, a living polymerization mechanism was indicated by an increase in UV adsorption when a thin film, cast from chloroform extraction of the reacted nanocomposite and then rinsed to remove unbound monomer and catalyst, was exposed to acetylene gas. This novel approach provides a unique route to synthesize mesostructured conjugated polymers and polymer/inorganic nanocomposites.

11:15 AM P7.8

PREPARATION OF SMART MESOPOROUS MATERIALS. Qiang Fu, G.V. Rama Rao, Yang Wu, S. Balamurugan, Gabriel P. Lopez, The University of New Mexico, Dept. of Chemical and Nuclear Engineering, Albuquerque, NM; L. Sklar, Dept. of Pathology, The University of New Mexico, Albuquerque, NM.

Mesoporous materials when integrated with stimuli responsive polymers which can undergo conformational changes to external stimuli such as pH, temperature, light and molecular recognition can provide a basis for the design and development of unique intelligent materials. We report grafting of a poly (N-isopropylacrylamide) (PNIPAAm), a thermo-responsive polymer, into the ordered pores of mesoporous silica matrices (films and particles) using atom transfer radical polymerization (ATRP).

PNIPAAm exhibits a lower critical solution temperature (LCST) at 32°C in water, below which it is in an expanded conformation and soluble in water. Above the LCST, PNIPAAm is in a compacted state and insoluble in water. Synthesis of mesoporous films and monodisperse microparticles was carried out through an acid catalyzed sol-gel process using a surfactant template approach. We used a non-ionic surfactant (Pluronic-P123) and a cationic surfactant (cetyltrimethyl ammonium bromide) for this study. X-ray diffraction and transmission electron microscopy studies on the films and particles confirmed the presence of an ordered porous structure before and after ATRP. The grafting of the polymer onto the pore surface was confirmed by drastic decrease in pore volume of the particles after ATRP as measured by nitrogen adsorption. Polymer grafted films showed a sharp change in the static contact angle at 30°C, which indicates the transition of the polymer from hydrophilic to hydrophobic state. Pore opening and closing due to contraction and expansion of PNIPAAm was studied by fluorescent dye uptake of particles by monitoring the fluorescence intensity in flow cytometry experiments. This new class of hybrid materials has potential applications in the areas of controlled-release systems, separations (chromatography and membranes), cell adhesion, regenerable biosensors and proteomic chips, and interfacial control of microfluidics in bio-MEMS devices.

11:30 AM P7.9

SELF-ASSEMBLED, CHIRAL POLYANILINE NANOCOMPOSITES AND MULTILAYERED THIN FILMS. Wenguang Li and Hsing-Lin Wang, Michelson Resource, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM.

Chiral conducting polymer nanocomposites composed of polyacrylic acid and polyaniline (PANI) were prepared via template-guided synthesis. In this work, we carried out detailed study of how temperature, template, molecular weight, and solvent affect the final morphology and properties of these nanocomposites. We found that the extent of interaction and stability of the template/monomer/acid complex (nanocomposite precursor) and population density of monomer surrounding the template, are crucial in determining the chirality of the nanocomposites. We then fabricate the multilayered thin films based on these water-dispersible polyaniline nanocomposites (PANINC) via spin-assembly method. Both doped and undoped PANINC were used to fabricate multilayer thin films up to 30 bilayers. Concurrent linear increase of both the amount of deposition and the optical activity in these thin films was observed. Spin-assembly introduces additional centrifugal force that allows the PANINC to align in a direction that is parallel to the substrate surface. AFM micrograph of a 20 PANINC/PDDA bilayer thin film shows a relatively smooth surface with a roughness of 300 nm, equivalent to the depth of 3-4 polyaniline nanoparticles. The above results suggest that spin-assembly is an ideal method for assembling multilayered thin films contain nanoparticles.

11:45 AM P7.10

PHOTOVOLTAIC CELLS MADE FROM SEMICONDUCTING POLYMERS IN MESOPOROUS TITANIA. Kevin Coakley, Yu-Xiang Liu, Michael McGehee, Stanford University, Dept. of Materials Science, Palo Alto, CA; Karen Frindell, Galen Stucky, University of California Santa Barbara, Dept. of Chemistry, Santa Barbara, CA.

In order to efficiently harvest excitons from conjugated polymers in organic/inorganic nanocomposite photovoltaic cells, an electron acceptor material is required to split the excitons before they recombine. Because the exciton diffusion length is typically on the order of 10 nm in conjugated polymers, the electron acceptor material must be structured on the nanometer length scale so that each exciton can diffuse to an interface prior to recombination. The acceptor material must also possess energy bands that are suitable for electron transfer from the polymer, and should have continuous pathways for the transport of electrons to the electrodes following charge transfer. Mesoporous titania (TiO_2) is an excellent candidate for use as an electron acceptor material because it is ordered on the nanometer length scale and has energy levels that are suitable for electron transfer from many conjugated polymers. Here we describe a procedure for making photovoltaic cells from mesoporous titania and regioregular poly(3-hexyl)thiophene (RR P3HT). We first fabricate thin films of mesoporous titania on a conducting glass substrate using block copolymer co-assembly. After the block copolymer is removed by calcination, the films possess a three-dimensional interconnected pore structure with exposed pores on the top surface of the film. In order to infiltrate the RR P3HT into the pores, films of the polymer are spun cast on top of the mesoporous film and heated at temperatures ranging from 100°C to 200°C. Higher infiltration temperatures result in larger amounts of infiltrated RR P3HT. Finally a gold top electrode is deposited using thermal evaporation. Photovoltaic cells made using this process have power efficiency greater than 1% under monochromatic illumination. Opportunities for further improvement of these photovoltaic cells will be discussed.

SESSION P8: SELF-ASSEMBLED POLYMERIC SYSTEMS II

Thursday Afternoon, April 24, 2003
Metropolitan III (Argent)

1:30 PM P8.1

TOWARDS THE DESIGN OF DIBLOCK COPOLYMERS FOR USE IN NOVEL CATALYTIC APPLICATIONS. Cheryl M. Stancik,

Stanford Univ, Dept of Chemical Engineering, Stanford, CA; Adrien R. Lavoie, Jan Schuetz, and Robert M. Waymouth, Stanford Univ, Dept of Chemistry, Stanford, CA; John A. Pople, Stanford Synchrotron Radiation Laboratory, Stanford, CA; Alice P. Gast, Dept of Chemical Engineering, MIT, Cambridge, MA.

We characterize a series of diblock copolymers using scattering techniques and work to build architecture-property relationships that will enable us to optimize their use for catalytic applications. These diblock copolymers comprise a polystyrene block and an imidazolium organic liquid functionalized polystyrene block. In a selective solvent, these copolymers self-assemble into micelles. Using both small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS), we demonstrate that the aggregation number and the size of the micelles (given by their radius of gyration, R_g) are correlated to the diblock copolymer architecture. Through dynamic light scattering (DLS) studies, we measure the hydrodynamic radius, R_h , of the micelles and investigate relationships between R_h and the diblock architecture. We demonstrate that the nature of the density distribution within these micelles, as given by R_g/R_h , indicates a micelle geometry with a compact core. To assess the capacity of the micellar core to act as a nano-reactor, we investigate the ability of micelles with an organic liquid functionality in the core to solvate free ionic liquid molecules where the bulk environment is a non-solvent for these molecules. Following addition of the ionic liquid molecules to micellar solutions, we see an increase in the micellar radii, indicating that ionic liquid molecules partition themselves to the cores of these micelles to escape the poor solvent environment of the bulk. We desire to use these organic liquid moieties in the novel environment of the micellar core for catalysis and present our preliminary findings in this direction.

1:45 PM P8.2

INKJET PRINTING OF SELF-ASSEMBLING POLYMERS.

Paul Calvert, University of Arizona, Dept. of Materials Science and Eng, Tucson, AZ.

inkjet printing allows patterns of polymers to be deposited from solution with layer thicknesses of about 100nm. By sequentially printing layers of reactive materials, gels and insoluble polymers can be patterned onto any surface. Sequential printing of aqueous solutions of epoxy and amine results in formation of insoluble hydrogels that can entrap proteins. Sequential printing of anionic and cationic polymers initially results in layers that rapidly redispense on immersion in water. If these layers are annealed overnight in a humid environment, they self-assemble to form insoluble layers. When thick, these layers usually show wrinkling where precipitation has occurred. It is clear that this process involves a complicated diffusion, complexation and precipitation process. If the first layer is a suspension of submicron ceramic particles dispersed with the anionic polymer, printing the cationic polymer and annealing results in a porous, bonded layer of particles. I will also discuss the extension of this method to self-assembling biopolymers.

2:00 PM *P8.3

TOWARDS MONODOMAINS OF POLYELECTROLYTIC AND COORDINATED COMB-SHAPED POLYMERIC SUPRAMOLECULES. Olli Ikkala, Olli Ikkala,

Helsinki Univ of Technology, Dept of Engineering Physics, Espoo, FINLAND; Gerrit ten Brinke, Univ of Groningen, Lab of Polymer Chemistry and Materials Science Center, Groningen, THE NETHERLANDS.

We have previously shown that hierarchical self-organization is achieved upon hydrogen bonding amphiphilic molecules to block copolymers. Imposed shear flow allows alignment of the locally self-organized structures. In this work, the concepts have been extended to charged polymers, which are relevant for eg. electro- and photoactive materials. We will first present poly(4-vinyl pyridine)-block-polystyrene diblock copolymers, where the pyridine groups have been protonated using toluene sulphonic acid and the resulting salt groups have been plasticized using alkylphenols. The weight fractions have been selected so that the plasticized salt groups microphase separate into cylindrical domains. We will present results where shear alignment leads to a monodomain of the self-organized structure, even showing a number of higher order reflections (T. Ruotsalainen et al). The anisotropic properties will be discussed. We will also discuss dielectric reflectors based on self-organized block polyelectrolytes (S. Valkama et al). In this case, the plasticization achieved by the oligomeric side chains facilitate the structure

formation in comparison to concepts utilizing blends of high polymers. Coordination bonding is a useful interactions to bond side chains to form polymeric supramolecules. We demonstrate concepts to achieve self-organized structures and structural hierarchies upon coordination of side chains to polymer chains, as well as phase tailoring. Finally, the concepts allow possibilities for mesoporous materials upon cleaving the coordinated side chains (H. Kosonen et al).

2:30 PM P8.4

NANOASSEMBLIES FROM BLOCK COPOLYMERS AND MULTIVALENT INORGANIC IONS. Nicolas Sanson, Frederic Bouyer, Corine Gerardin, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, FRANCE.

Hydrophilic diblock copolymers, which contain an ionizable block and a neutral block can form nano-assemblies when they are mixed with oppositely charged entities. Water-soluble anionic-neutral block copolymers, such as PMMA-b-PEO, are known to form Polyion Complex Micelles when mixed with oppositely charged surfactants, polyelectrolytes or block copolymers. The case of mixtures of block copolymers and inorganic polyelectrolytes was not investigated in details yet. In that case, macromolecular complexes are also spontaneously produced during mixing of the block copolymers with the inorganic polyions. The spontaneous formation of big hybrid objects is observed, due to complexation of the inorganic ions by the metal-binding block. The small cationic inorganic entities which induce copolymer micellization are simply metal salts such as Al(3+) or Cu(2+) or polycationic clusters such as Al13(7+) or Al30(18+). The block copolymers used in this study are polyacrylic acid (PAA)-polyhydroxyethylacrylate (PHEA). The aggregate size, morphology and nanostructure have been investigated using small angle neutron scattering, dynamic light scattering and cryogenic transmission electron microscopy. The aggregate formation has also been followed using pH and conductivity measurements, IR and NMR spectroscopy and electrophoretic measurements of the zeta-potentials. It was shown that, for some specific relative block lengths, well-defined monodisperse spherical core-corona objects form. The micellar core is dense and spherical with a sharp interface, it is composed of the inorganic-polymer complex and the neutral blocks form a diffuse polymeric corona that brings steric stabilization to the system. The micelles so formed are very stable and they exhibit some properties of amphiphilic block copolymers on one hand and of polyelectrolytes on the other hand. Finally, those hybrid micelles represent promising supramolecular precursors of tailored architecture for nanostructured materials.

2:45 PM P8.5

IONICALLY SELF-ASSEMBLED POLYMER ELECTROCHROMIC DEVICES. J.R. Heflin, J.A. Janik, C. Choi, S. Yancey,

Virginia Tech, Dept of Physics, Blacksburg, VA; P. Stevenson, N. Short, Y. Liu, Luna Innovations, Blacksburg, VA; H. Wang, H.W. Gibson, Virginia Tech, Dept of Chemistry, Blacksburg, VA.

The electrochromic effect results from the motion of ions into and out of an active material, resulting in reversible changes in electronic structure and absorption spectra. We report studies of electrochromic devices fabricated from ionically self-assembled monolayers (ISAMs), in which fast switching rates are achieved by nanoscale control of film composition. ISAMs, fabricated by alternate adsorption of cationic and anionic components, yield exceptionally homogeneous thin films with subnanometer control of the thickness and relative spatial location of the component materials. ISAM films were adsorbed onto indium tin oxide-coated glass substrates using electrochromic polymers, such as polyaniline(emeraldine base) (PANI) and poly-viologen, with the ionic conductor poly(2-acrylamido 2-methyl propane sulfonic acid) (PAMPS). Solid-state electrochromic devices, fabricated by sandwiching identical ISAM films with a conducting interlayer, exhibited large, reversible absorbance changes with application of 1.0 V. Devices in which PANI and PAMPS are placed in alternating layers showed larger magnitude absorbance changes and faster response times than those in which layers of PANI and poly(methacrylic acid) are followed by poly(allylamine hydrochloride) and PAMPS. Rise and fall times shorter than 50 milliseconds have been observed in the former devices. We describe systematic studies of the magnitude of the absorbance change and the switching speed as a function of nanoscale thickness and composition.

3:30 PM *P8.6

BLOCK-COPOLYMER-FREE APPROACHES TO POLYMERIC MICELLES AND HOLLOW SPHERES. Ming Jiang, Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, CHINA.

In recent years, progresses have been achieved in this laboratory in constructing self-assembled micelles, and hollow spheres rather than irregular aggregates by using polymers with interaction sites via some

special but simple procedures. Differing from the micelles made of block copolymers in which covalent bonds always exist between the core and shell, a series of non-covalently connected micelles (NCCM) based on homopolymer pairs with hydrogen bonding were produced. The average hydrodynamic diameters of the micelles were mostly in the range of 50nm to 300nm. We also found that hollow spheres could be directly obtained by simply mixing coil-like and rod-like homopolymers in their common solvent. Recently, It was found that the polymer pair of poly(ϵ -caprolactone) (PCL) and a graft-like copolymer having short PCL branches could self-assemble into micelles in water as well. After shell-crosslinking and core-degradation by enzyme, hollow spheres were obtained. In addition, we found that hydroxyethyl cellulose-graft-Polyacrylic acid (HEC-g-PAA) formed micelles in water by simply decreasing the pH of the medium. Crosslinking the PAA chains at the periphery part of the micellar core could efficiently lock the integrality of the micelles. The resultant micelles transformed into hollow spheres as the pH increased. Both the micellization and the transition from micelles to hollow spheres are found to be reversible. The hollow spheres show on-off character at the pH around 3. As all these new procedures are simple in practice using common and non-expensive polymer products, they are promising in further applications.

4:00 PM P8.7

ONE- AND TWO-DIMENSIONAL SEMICONDUCTING NANOSTRUCTURES OBTAINED BY SELF-ASSEMBLING PROCESSES OF CONJUGATED OLIGOMERS. Philippe Leclere, University of Mons-Hainaut/Materia Nova, Mons, BELGIUM; M. Surin, University of Mons-Hainaut, Mons, BELGIUM; O. Henze, IRC, Durham, UNITED KINGDOM; W.J. Feast, IRC, Durham, UNITED KINGDOM; F. Biscarini, CNR, Bologna, ITALY; E.W. Meijer, Technical University Eindhoven, THE NETHERLANDS; A.C. Grimsdale, MPI-P, Mainz, GERMANY; K. Muellen, MPI-P, Mainz, GERMANY; J.L. Bredas, Dept of Chemistry, University of Arizona, Tucson, AZ; and R. Lazzaroni, University of Mons-Hainaut, Mons, BELGIUM.

The solid-state properties of organic electronic materials are determined not only by those of individual molecules but also by those of ensembles of molecules. The ability to control the architectures of these ensembles is thus essential in optimising the properties of conjugated materials for use in electronic devices (light emitting diodes, field effect transistors, solar cells, ...) and is primordial for potential technological applications in nanoelectronics. For instance, a clear correlation between the molecular structures, the mesoscopic structures, as shown by the film morphologies, and the optical, in particular the luminescent properties, has been recently established. Self-assembly of synthetic materials has been recently proposed as a means of fabrication of nano-devices. In this domain, the ordering of block copolymers and oligomers leads to the formation of well-defined nanostructures. Here, we report on the observation by atomic force microscopy (AFM) of 1D and 2D nanoscale architectures obtained in the solid-state from solutions of molecularly-dissolved conjugated block copolymers or oligomers, and demonstrate that the conjugated molecules can organize onto a surface over lengthscales from nanometers to several microns, forming semiconducting fibrils by π -stacking processes. The presence of bulky side chains or chiral centers (located either along the non-conjugated segment or on a substituent of the conjugated segment) is also drastically affecting the final morphology. It appears that the formation of fibrils is predominant only when the molecular interactions are stronger than the molecule/surface interactions. When they are weaker, the unidimensional supramolecular organization is prevented and non-organized or 2D-morphologies (like crepes or tiles) dominate. These facts strongly suggest that the nature of the surface is one key parameter governing the formation of the supramolecular assemblies.

4:15 PM P8.8

EFFECT OF CATION SIZE AND VALENCY ON THE IONIC NANOAGGREGATES IN POLY(STYRENE-RAN-METHACRYLIC ACID) IONOMERS. Brian P. Kirkmeyer, Karen I. Winey, Univ of Pennsylvania, Dept of Materials Science and Engineering, Philadelphia, PA; Joon-Seop Kim, Chosun Univ, Kwangju, KOREA.

Previous STEM studies of fully-neutralized poly(styrene-ran-methacrylic acid) (SMAA) ionomers have shown spherical or vesicular aggregates when neutralized with Zn or Cs, respectively. The current study probes the effects of cation size and valency on the morphology of the ionic aggregates by examining SMAA neutralized with cations from Groups 1 and 2 of the periodic table. Results to date suggest that the cation size is more significant than the cation valency. For example, fully neutralized SMAA ionomers exhibit spherical aggregates with Na⁺ (ionic radius 0.095 nm) and vesicular aggregates with Cs⁺ (ionic radius 0.169 nm). In addition to the shape of the ionic aggregates, their size and number density are measured to further understand the influence of the cations on the ionic aggregates. Complimentary studies are underway

in our group using poly(ethylene-ran-methacrylic acid) neutralized with same range of cations, as well as computer simulations and rheological measurements.

4:30 PM P8.9

SELF-CONSISTENT FIELD THEORY AS A PREDICTIVE TOOL FOR SELF-ASSEMBLED MATERIALS. Kim Rasmussen, Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM.

By way of a number of examples we describe how self-consistent field theory is a general and powerful computational tool for self-assembled materials. Using multiblock copolymers and lipid monolayers as example we show that self-consistent field theory can yield more than morphological information. We demonstrate how information on the molecular level in terms of molecules bridging domains, molecular packing abilities etc. can be obtained and we correlates these theoretical findings experimental results.

4:45 PM P8.10

DYNAMICS AND RHEOLOGY OF GLASSY MICELLAR BLOCK POLYELECTROLYTES. Julien Grandjean, Ahmed Mourchid, CNRS-Rhodia, Complex Fluids Lab., Cranbury, NJ.

We present rheology and dynamic light scattering for micellar solutions of polystyrene-poly(acrylic acid) block copolymers. We tune the interactions in this system by inducing attraction so that the micelles can be regarded as sticky hard spheres. These systems form gels at high effective micellar volume fractions, suggestive of disordered colloidal glasses. At the gel point, the viscoelastic moduli follow the scaling power law predicted for G' and G'' by classical percolation theory. This scaling can be due either to formation of a percolated network or a pre-transitional glassy phase. However, the dynamics nearby the transition from the liquid phase to the viscoelastic phase have similarities to those of hard sphere colloidal suspensions at the glass transition. Our rheological and dynamic light scattering results agree well with the detailed predictions of the mode coupling theory: 1) without attractive forces the system evolves as a glassy material showing generic behavior. 2) Switching on attraction between the micelles increases the dynamics of the micelles. The rheology follows this speeding up; in other words the melting of the glass triggered by the re-entrant transition decreases the elasticity. 3) Increasing attraction further, a much more pronounced stretched relaxation of the dynamics occurs. This phenomenon takes place when the system gets close to the intersection of the liquid-repulsive glass transition and the liquid-attractive glass transition. In this region of the phase diagram, the microscopic dynamics of the micelles is well described by a logarithmic decay of the correlation function that starts in the liquid phase and continues in the glass phase expanding over several time decades.

SESSION P9: POSTER SESSION
SYNTHESIS, ASSEMBLY, AND APPLICATION OF
NANO-BUILDING BLOCKS
Thursday Evening, April 24, 2003
8:00 PM
Golden Gate (Marriott)

P9.1

FABRICATION OF SELF-ASSEMBLED, SIZE-GRADED Si QUANTUM DOTS BY PULSED LASER DEPOSITION. D.O. Henderson, R.H. Wu, R Mu, and A. Ueda, Chemical Physics Laboratory, Department of Physics, Fisk University, Nashville, TN; B. Vlahovic, Department of Physics, North Carolina Central University, Durham, NC; M. Jaksic, Rudjer Boskovic Institute, Zagreb, CROATIA.

Size graded, self-assembled silicon quantum dot structures were synthesized by pulsed laser ablation using the output of the second harmonic of a picosecond Nd:YAG laser. The ablation experiments were performed under vacuum and in the presence of 0.5 to 1.0 torr of He and the laser energy was varied from 0.8 to 1.2 mJ. The samples were characterized by atomic force microscopy, which indicated that the silicon quantum dots increased in size with an increase in the pressure of the backing gas and the laser energy. The optical absorption spectra showed an increase in the band edge absorption with a decrease in the quantum dots size, which is consistent with the predictions of quantum confinement models. Also, spatially resolved optical absorption measurements showed quantum dots formed near the plume center absorbed at lower energies than the quantum dots near the wings of the plume. Absorption measurements made between these two extrema (in the direction from the plume center to the wings) revealed a continuous blue shift in the band edge. The continuous blue shift is attributed to a continuous decrease in the quantum dot size.

P9.2

SELF-ASSEMBLED NANOSTRUCTURE IN SPUTTERED Co-X (X=Cr, Pd) ALLOY FILMS. Kiyung Lee, Ohsung Song, Seonghwee Cheong, The University of Seoul, Dept of Materials Science and Engineering, Seoul, KOREA.

Advances in magnetic recording technology have resulted primarily from proportional scaling of each individual storage bit. These trends have driven the development of new magnetic thin film media with smaller grains, high coercivity, low magnetization and minimal magnetic exchange coupling between neighboring grains. Today, the grain size of Co-X alloy based advanced recording media has been reduced to dimensions close to the onset of superparamagnetic behavior with self-assembled mechanism. Especially, Co-X alloy thin films that have self-assembled magnetic nanoparticle arrays are promising for high-density information storage media in information era. We investigated the nano-microstructure and magnetic property of Co-Cr, Co-Cr-Pd and Co-Pd alloy system. We investigated the saturation magnetization (M_s), coercivity, and remanence of the Co-X alloy films using a vibration sample magnetometer (VSM) by varying content of alloy elements at the substrate temperatures of 30° and 200°, respectively. Microstructure and Co-X alloy films are probed by a transmission electron microscope (TEM) and an energy dispersive spectroscopy (EDS). We confirmed that self-assembled nanostructure (SANS) occurred in Co-22%Cr films at the elevated substrate temperatures. Our results imply that Co-22%Cr alloy films are promising for high-density perpendicular magnetic recording media with their perpendicular anisotropy and appropriate coercivity of 3000 Oe. In Co-Cr-Pd films, Co-enriched phase is self-assembled inside the grains as Pd selectively reacts with Cr near grain boundary, which leads to M_s enhancement. Co-Pd films deposited at the room temperature showed suitable saturation magnetization, remanence and coercivity for the perpendicular recording, which implies the occurrence of SANS. Such SANS in Co-X magnetic thin films is appropriate to high-density recording of 100 Gbit/in².

P9.3

NANOPATTERNING BY ELECTROSTATIC DIP-PEN NANOLITHOGRAPHY. Laura Sowards, Rajesh Naik, Morley Stone, Materials and Manufacturing Directorate, Air Force Research Labs, Wright-Patterson Air Force Base, Dayton, OH.

In this work, we demonstrate that biological molecules can be deposited by Dip-pen Nanolithography (DPN) using electrostatic binding techniques rather than the traditional affinity linkage of thiol to gold. The primary factors governing electrostatic interactions are the charges on the biomolecule (determined by its isoelectric point, pH of the buffer, etc.) and the substrate. We have utilized these electrostatic interactions to achieve nanoscale deposition of peptides directly onto molecularly smooth surfaces like mica and silica using DPN. This type of interaction, which enables attachment of biomolecules without chemical modifications thus preserving their native structure and properties, is similar to layer-by-layer electrostatic assembly techniques(1), yet it allows for the specific patterning of molecules. Traditional electrostatic assembly (ESA) results in the entire substrate surface being coated with molecules while electrostatic DPN deposits a monolayer of molecules in precise locations to allow resolution at the nanoscale. Electrostatic assembly could be used as a method to build additional layers onto the initial electrostatic DPN deposited pattern. (1)Decher, G. Science, (1997), 277, 1232-1237.

P9.4

ELECTRON MICROSCOPY STUDY OF SUBMICRON SIZE ANTIFERROMAGNETIC KMnF₃ NANOPARTICLES AND THEIR SELF-ASSEMBLY. Weilie L. Zhou and Rubi Garcia, Advanced Materials Research Institute, University of New Orleans, LA.

Nanocrystals of KMnF₃ have been synthesized by using reverse micelle method. The synthesis and nanostructures of the nanocrystals were studied by field emission electron microscopy and transmission electron microscopy. KMnF₃ nanocrystals synthesized at room temperature are of cubic shape with 100 nm and consist of KMnF₃ nanocrystallites with 10-15 nm. As the reaction time increase the nanocrystals finally turn into perfect cubic nanocrystals. Spherical beads composed of KMnF₃ nanocrystallites were observed at low temperature synthesis. As the reaction continues, the spherical particles grow larger, but are not forming the characteristic cubic shape of KMnF₃ nanoparticles. At this temperature it is believed that the energy present in the system is not enough to allow for the optimum growth of the KMnF₃ crystals. Even as they grow larger, there is no evidence of homogeneous crystal morphology as seen in the room temperature samples. Cubic shape KMnF₃ nanocrystals were self-assembled into large area self-assembling patterns.

P9.5

ARCHITECTURAL ASSEMBLY OF COBALT NANOPARTICLE

MONOLAYER ON FUNCTIONALIZED SILICON SURFACE.

Sung-Soo Bae, Do Kyung Lim, Jong-II Park, Sehun Kim, Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Daejeon, SOUTH KOREA; Jinwoo Cheon, Department of Chemistry, College of Science, Yonsei University, Seoul, SOUTH KOREA.

We introduce a novel versatile strategy to make a monolayer assembly of Co-nanoparticle on a Si(111) surface via the covalent linkage of terminal functional groups between the Si surface and the nanoparticles. The Co-nanoparticles assembled on the hydroxyl-terminated Si surface exhibit 2-D island networks with locally ordered arrays. On the other hand, the Co-nanoparticles on the aminopropyl-terminated Si surface show an individual and random distribution over a wide area of surface. This general strategy provides strong nanoparticle-substrate chemical bonding, and high number density. Also, a variety of distributions of nanoparticles is possible by controlling reaction conditions. Furthermore, using the microcontact printing method together with the covalent linkage method, we have achieved a selectively patterned monolayer assembly of Co-nanoparticles on the micropatterned Si surface. The patterned structures consist of two regions which are the monolayer assembly of nanoparticles and the inert long alkyl chains, respectively. We demonstrate that these methods for the selective monolayer assembly of nanoparticles can be used for preparing nano-building blocks for future nanoelectronic devices.

P9.6

SYNTHESIS AND CONTROL OF GLOBULAR PLATINUM-PARTICLE NANOASSEMBLIES. Yujiang Song, Xiaolin Lu, Yi Yang, Univ of New Mexico, Dept of Chemistry and Chemical and Nuclear Engineering, Albuquerque, NM; Craig J. Medforth, Frank van Swol, John A. Shelnutt, Sandia National Labs, Albuquerque, NM.

The synthesis of platinum nanostructures or nanoassemblies, other than nanoparticles and nanowires, are rare. We have found that globular clusters of platinum nanoparticles can be formed either by photocatalytic or chemical reduction of Pt(II) complex from aqueous SDS, Brij35, or Brij58 surfactant solutions under ambient conditions using ascorbic acid as the electron donor. The photocatalyst is a tin(IV) porphyrin complex. The nanoassemblies of 3-nm Pt particles are porous and single-crystalline, i.e., the 3-nm nanocrystals making up the assemblies are crystallographically aligned and joined together into a robust porous globular nanostructure. The synthesis of the nanoassemblies can be controlled by varying light intensity and exposure time, photocatalyst concentration, and pH conditions. At pH 1, uniform sized globular nanoassemblies are formed by photocatalytic reduction mediated by Sn porphyrin in micelles under intense incandescent light illumination. At pH 3, however, ascorbate formation is significant, and 3-nm Pt particles are formed at a slow rate by this strong reductant, with or without photocatalyst present. These Pt nanoparticles catalyze fast reduction of Pt(II) complex by ascorbate, thus forming nucleation centers for rapid growth of nanoparticle assemblies. The nucleation centers are formed by the slow reaction over the entire 15-minute reaction time and lead to nanoassembly sizes ranging from ~10 to 150 nm in diameter. However, uniform-sized clusters can be synthesized without photocatalyst by adding Pt-nanoparticles as nucleation centers to initiate and synchronize the catalytic reduction process. The concentration of nanoparticle nucleation centers, and thus the uniform nanoassembly size, can also be controlled by photocatalytic generation of the nucleation centers. This is accomplished by an initial short exposure (10-60 seconds) to bright light in the presence of Sn porphyrin. In addition, nanoassembly size can be controlled by porphyrin concentration when the reaction solution is continuously exposed to intense light.

P9.7

PRODUCTION OF NANOSTRUCTURES UNDER ULTRATURBULENT COLLISION REACTION CONDITIONS - APPLICATION TO CATALYSTS, SUPERCONDUCTORS, CMP ABRASIVES, CERAMICS AND OTHER NANOPARTICLES. Irwin J. Gruverman and Jeffrey Thumm.

The development, operation and applications of a novel continuous chemical reactor system are described. The system (known as a Multiple Stream Mixer/Reactor or MMR) produces nanoparticles by direct precipitation from two or more reactant solution streams, in an extreme energy density ultraturbulent collision reaction region. Sensors and a control system are employed to assure constant mixing conditions and desired stoichiometry in the reaction region. The interaction chamber is designed to allow macro-, meso-, and micro-mixing during the reaction process. This allows control of product purity, yield, size, size distribution and phase purity. Typical nanoparticle diameters in the one to ten nanometer range are achievable, with tight size distribution. The MMR can be scaled from development quantities to tons/hour for production applications. Capital cost, operating cost and energy consumption appear favorable

relative to other reaction technologies. Examples of successful demonstration programs are presented.

P9.8

STRUCTURE OF SELF-ASSEMBLED MAGNETIC FePtCu NANOPARTICLES ARRAYS. Xiangcheng Sun and D.E. Nikles, Center for Materials for Information Technology (MINT), University of Alabama, Tuscaloosa AL; J. Li, X.D. Bai, Z.L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA; M. Shamsuzzoha, Department of Metallurgical & Materials Engineering, University of Alabama, Tuscaloosa AL.

Controlled self-assembly of magnetic nanoparticles has stimulated great interest recently as it may offer a convenient tool for magnetic nanodevice fabrication. A tightly packed assembly of exchange-decoupled magnetic nanoparticles may serve as future ultrahigh-density data storage media. In this study, a series of $\text{Fe}_x\text{Pt}_y\text{Cu}_{100-x-y}$ nanoparticles were synthesized by chemically solution-phase reduction of platinum and copper reagents and thermal decomposition of iron pentacarbonyl in the presence of stabilizers oleic acid and oleyl amine. As-prepared particles have a chemically disordered face-centered cubic (fcc) lattice with an average diameter of 3.5 nm and are superparamagnetic. The particle size, and the corresponding size distribution were controlled by varying the organic surfactant (oleic acids etc.), its concentration, and the reaction temperature. These particles were well dispersed in hydrocarbon solvents and self-assembled into two or three dimensions particles arrays with a variety of close-packing arrangements. Domain of monolayer, bilayers and multilayers of particles arrays were frequently detected in TEM specimens. Both cubic close-packed (ccp) and honeycomb arrays were also uniquely observed by conventional and high resolution transmission electron microscopy, and further confirmed in terms of projected potential image simulation. More interestingly, these highly ordered self-assembled FePtCu particles appear to keep their orderly packing even after in-situ thermally annealed treatment, and each particle exhibiting chemically ordered L1_0 phase. It was also demonstrated that the controlled organic surfactant layer (organic capping) play a crucial role in determining assembly dimensions and symmetry as well as particles packing arrays.

P9.9

Abstract Withdrawn.

P9.10

STRUCTURAL ANALYSIS ON SELF-ASSEMBLED MOLYBDENUM SULFIDES NANOPHASES CATALYSTS. Xiangcheng Sun and David E. Nikles, Center for Materials for Information Technology (MINT), The University of Alabama, Tuscaloosa AL; Y.Q. Wang, Beijing Lab of Electron Microscopy, Institute of Physics, Chinese Academy of Science, Beijing, P.R. CHINA.

MoS_2 possesses outstanding properties toward hydrodesulfurization (HDS) reactions. It had been found that the activity depended on the relative amount of edge Mo atoms where sulfur vacancies can be easily formed. And the activity of MoS_2 depends not only on the particle size but also on the number of layers. Self-assembled molybdenum sulfide nanophases catalysts were synthesized successfully by hydrothermal reduction approach. A series of high-resolution transmission electron microscope (HREM) images showed that MoS_2 grains were made of deformed bundles of (002) planes. The large flexibility of MoS_2 planes for deformation reduced contact between grains, avoiding pore formation during the hydrodesulfurization process. HREM lattice fringes are basically separated by 0.6 nm, they correspond to the spacing between (002) basal planes of MoS_2 . These planes are bend, crystal bending favors the formation of defect, which is important to improve the reaction ability on photo-electrochemistry. Some specific structures evidences of restacked structure and the tip of nanotube shape of these MoS_2 catalysts are also observed by using high resolution electron microscopy (HREM) and selected area electron diffraction (SAED). These novel structure features give good improvements on its catalytic properties.

P9.11

SELF-ORGANIZATION OF SILICON DOTS GROWN FROM THE THERMAL DECOMPOSITION OF HSiO₃/2 GELS. Jerome Rouquette, Monique Pauthe, Michel Ramonda, Bernard Gil, Université de Montpellier 2, Montpellier, FRANCE.

We report the possibility to easily produce an anisotropic self-organization of silicon dots on a silicon substrate. Our method is based on the thermal decomposition under static vacuum of an $\text{HSiO}_3/2$ gel placed near a (001)-oriented silicon substrate. The formation of dots occurs for temperature heating treatments of the gel higher than 500°C, and orientation of the dots occurs along the $\langle \pm 110 \rangle$ directions of the silicon substrate when the experiment is done at temperatures higher than 800°C. Advantage of the anisotropy

of the coalescence of these dots can be taken for forming zero-cost silicon nanochains and nanowires.

P9.12

CHARACTERIZATION OF NANO-SIZE INDIUM CLUSTER IN InGa_N/Ga_N MULTIPLE QUANTUM WELLS WITH HIGH INDIUM COMPOSITION. Hyung Koun Cho and Dong-A Univ, Dept of Metallurgical Engineering, Busan, KOREA; Jeong Yong Lee, KAIST, Dept of Material Science and Engineering, Daejeon, KOREA.

To achieve longer wavelength light emission diodes (LEDs), higher indium composition in $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ MQW structures as an active material is required. An increase in indium composition results in the large lattice mismatch between InGa_N wells and Ga_N barriers. Below the critical thickness indium cluster induced by misfit strain is observed like quantum dots. In this experimental, we report the formation of nano-size indium clusters in InGa_N/Ga_N multiple quantum wells with high indium composition. Indium cluster confirmed by high-resolution transmission electron microscopy results in the redshift of the emission peak and the increase of the integrated photoluminescence (PL) intensity. We found that strong carrier localization in indium cluster induces the increases of the activation energy of PL integrated intensity, the temperature independence of PL decay profiles, and the intensity fluctuation of the cathodoluminescence images. All these observations suggest structurally and optically that the improved emission properties in the InGa_N/Ga_N multiple quantum well with high indium composition are associated with the localized states in the strain-induced indium cluster.

P9.13

SELF-ASSEMBLY OF AROMATIC TETRAAZAMACROCYCLIC COMPLEXES ON SINGLE-WALLED CARBON NANOTUBES. Elena V. Basiuk (Golovataya Dzhybeeva) and Jose M. Saniger, Universidad Nacional Autonoma de Mexico, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Mexico D.F., MEXICO; Elena V. Rybak-Akimova, Tufts Univ, Dept of Chemistry, Medford, MA; Vladimir A. Basiuk, Universidad Nacional Autonoma de Mexico, Instituto de Ciencias Nucleares, Mexico D.F., MEXICO; Dwight Acosta-Najarro, Universidad Nacional Autonoma de Mexico, Instituto de Fisica, Mexico D.F., MEXICO.

Chemical derivatization is an efficient tool to modify chemical and physical properties of carbon nanotubes (CNTs) and to expand their application areas. Among the compounds of special interest as reagents for CNT modification are metal complexes, in particular those having magnetic properties. All the existing methods of chemical modification of CNTs can be divided in two groups, depending on whether functionalizing moieties are introduced onto the nanotube tips or sidewalls. The latter approach offers wider opportunities to change CNT properties. In turn, the modification can rely upon either covalent bond formation, or adsorption on CNT sidewalls. As a preliminary study for the possibility of reversible modification of CNT walls with metal complexes, we studied interaction of Ni(II) and Cu(II) complexes of tetramethyltetraazaannulene (TMTAA) with single-walled carbon nanotubes (SWNTs). SWNTs strongly adsorb NiTMTAA and CuTMTAA from ethanol solutions, with SWNT:complex mass ratio of ca. 5:4. According to the results of molecular mechanics modeling, this corresponds to a dense monolayer coverage. A saddle-shaped conformation of the macrocyclic complexes helps their better accommodation on the cylindrical nanotube walls, resulting in a highly ordered molecular assembly. The materials synthesized were characterized by IR, UV-Vis and EPR spectroscopy, as well as electron microscopic methods.

P9.14

A NOVEL SELECTIVE DEPOSITION USING SOFT LITHOGRAPHY SELF-ASSEMBLED MONOLAYERS. Daekyun Jeong, Juwhan Park, Nohheon Park, Hyunjung Shin, JaeGab Lee, Myung-Mo Sung^a, Jiyoung Kim, Department of Advanced Materials Engineering, Kookmin University. ^aDepartment of Chemistry, Kookmin University, SungBuk-Gu, Seoul, KOREA.

Soft lithographic techniques such as micro-contact printing offer an attractive alternative to conventional lithography. The micro-contact printing is a straightforward, low-cost and high throughput method of patterning which can cover large areas in a single stamping operation on nonplanar surfaces without needs of clean room environments. Especially, the contact printing is capable of transferring self-assembled monolayer (SAM) pattern with sub-micron feature sizes. The SAM patterns form nanoscopic film regions terminated by chemical functionalities predetermined by the structure of the "ink" employed. Long-chain alkyltrichlorosilanes (RSiCl_3) are typical inks for oxide substrates (such as SiO_2/Si substrate) with the $-\text{SiCl}_3$ groups reacting rapidly with surface hydroxyl functionalities. The hydrophobic long chain alkyl groups form densely packed monolayers, with interchain spacings largely determined by van der Waals forces.

Thus, the pattern transfer creates a hydrophobic surface in the stamped area, leaving the ink-free hydrophilic surface unmodified. A novel selective deposition technique has been developed on the two distinct surface property areas, with and without the SAM layers, when thin films growth mechanism is dominated by a surface reaction. In this study, we fabricated Cu/ZrO₂/Si stacked structure capacitors using the novel selective deposition technique. Si (100) wafers were cleaned by RCA cleaning, and then we patterned SAMs of OTS (CH₃(CH₂)₁₇SiCl₃) by micro-contact printing. Since mechanism of atomic layer deposition (ALD) is mainly a surface reaction, zirconium oxide thin films were selectively grown using zirconium t-butoxide and water by ALD. Even though a deposition tool for Cu is not an ALD, Cu films were selectively deposited using MOCVD because Cu films were not nucleated on the OTS layer at the deposition temperature lower than 200°C. In this presentation, we will report the effects of process parameters on the selectivity of deposition. In addition, we will mention materials and electrical characteristics of the Cu/ZrO₂/Si structure capacitors which were fabricated without any etching process.

P9.15

IRON-PHTHALOCYANINE MODIFIED ELECTRODES FOR DETECTING DOPAMINE. V. Zucolotto and M. Ferreira, University of Sao Paulo, Dept of Physics and Materials Science, Sao Carlos, SP, BRAZIL; M.R. Cordeiro, Federal Univ of Sao Carlos, Dept of Chemistry, Sao Carlos, SP, BRAZIL; C.J.L. Constantino, Univ of Sao Paulo State, Presidente Prudente, SP, Brazil; Débora T. Balogh, University of Sao Paulo, Dept of Physics and Materials Science, Sao Carlos, SP, BRAZIL; W.C. Moreira, Federal Univ of Sao Carlos, Dept of Chemistry, Sao Carlos, SP, BRAZIL; Osvaldo N. Oliveira Jr., University of Sao Paulo, Dept of Physics and Materials Science, Sao Carlos, SP, BRAZIL.

Nanostructured phthalocyanine-modified electrodes were fabricated using the electrostatic layer-by-layer (LBL) technique, where iron tetrasulfonated phthalocyanine (FeTsPc) layers were alternated with poly(allylamine hydrochloride) (PAH) or water-soluble polyaniline (PANI) onto ITO-covered glass substrates. The multilayer formation was monitored via UV-Vis spectroscopy by measuring the increase in the Q-Band of FeTsPc at 676 nm. Film thickness of PAH/FeTsPc films was estimated by profilometry as ca. 10 Å per bilayer. Fourier transform infrared spectroscopy and UV-Vis absorption suggested specific interactions between FeTsPc and PAH, such as those between SO₃-NH which we believe to bind PAH and FeTsPc. There is also evidence of interactions between unprotonated amine groups of PAH and the coordinating metal of the phthalocyanine. Cyclic voltammograms for a 50-bilayer PAH/FeTsPc film at 50 mV/s (vs Ag/Ag⁺) showed reproducible pairs of oxidation-reduction peaks at 1.07 V and 0.81 V, respectively. The peaks corresponding to the FeTsPc redox process did not appear in the voltammograms for PANI/FeTsPc LBL films, which contained only the PANI oxidation-reduction peaks. In the presence of dopamine the PANI/FeTsPc films showed additional redox peaks at 0.207 and 0.021 V resulting from interaction of dopamine and FeTsPc. The presence of dopamine caused passivation of PAH/FeTsPc electrodes. In this case, we believe that dopamine-FeTsPc interactions do not occur due to the coordination of iron coordinating atoms to NH₂ groups of PAH.

P9.16

Abstract Withdrawn.

P9.17

NANOPATTERNED Si(001) SUBSTRATES AS TEMPLATES FOR QUANTUM DOT GROWTH. A. Ney, C. Pampuch, J.J. Schulz, L. Perepelitchenko, R. Koch, Paul-Drude-Institut für Festkörperelektronik, Berlin, GERMANY.

It has been shown recently, that the formation of GeSi quantum dots on Si(001) is strongly affected by the surface properties of the substrate [1]. With an increasing number of missing dimer vacancies the growth mode can even change from a Stranski-Krastanow to a kinetic 3D island growth mode. Here we report on detailed investigations of different preparation procedures of Si(001), namely the conventional high temperature procedure employed for commercial wafers, and Shiraki-type samples which require only low temperature treatment. The latter method yields an atomically flat Si(001) (2×1) surface, however, with a defect concentration depending on the respective preparation conditions. Furthermore, repeated flashing yields a (2×n) reconstructed surface consisting of well-ordered self-assembled trenches of missing dimers, similar to the ones discussed controversially in the previous literature [2]. From our results we can clearly exclude contaminants (e.g. nickel or oxygen) to be involved.

[1] R. Koch, G. Wedler, J.J. Schulz, and B. Wassermann, Phys. Rev. Lett. 87, 136104 (2001).

[2] A.R. Smith, F.K. Men, K.-J. Chao, Z. Zhang, and C.K. Shih, J. Vac. Sci. Technol. B 14, 909 (1996).

P9.18

TRANSFER OF MONODISPERSE MAGNETIC IRON OXIDE NANOPARTICLES INTO AQUEOUS MEDIA AND COOPERATIVE ASSEMBLY WITH BLOCK COPOLYPEPTIDES. Stephanie Grancharov, IBM Research, Yorktown Heights, NY and Columbia University, Dept of Applied Physics, New York, NY; Larken Euliss, IBM Research, Yorktown Heights, NY and UCSB, Dept of Chemistry, Santa Barbara, CA; Stephen O'Brien, Columbia University, Dept of Applied Physics, New York, NY; Galen Stucky, UCSB, Dept of Chemistry, Santa Barbara, CA; Christopher B. Murray, IBM Research, Yorktown Heights, NY; Glenn A. Held, IBM Research, Yorktown Heights, NY.

We demonstrate that highly crystalline, monodisperse maghemite nanoparticles, which are synthesized in organic solvents, can be effectively transferred into an aqueous medium using an ammonium salt in basic conditions. The nanocrystals remain monodisperse as characterized by TEM and XRD, as well as superparamagnetic as determined through SQUID measurements. When the aqueous iron oxide is combined with the block copolypeptide poly(ethyleneglycol-lysine₁₀₀aspartic acid₃₀), the nanoparticles are self-assembled into round clusters each comprised of approximately 40 nanoparticles. Organization of biologically compatible polymers with magnetic nanoparticles in the future may lead to useful biological applications such as imaging and drug delivery.

P9.19

DEPOSITION OF SMALL DIAMETER CARBON NANOTUBES ON THE IRON-ALUMINA CATALYSTS. Weizhong Qian, Chen Lin, Fei Wei, Guohua Luo, Dept of Chemical Engineering, Tsinghua University, Beijing, CHINA.

Carbon nanotubes are prepared from the ethylene decomposition by iron-alumina catalysts. The relationship between the diameter distribution of as-grown CNTs and the molar ratio of iron to alumina is widely investigated by using TEM, XRD. It is found that, when this ratio is in the range of 1:2 to 2:1, carbon nanotubes with average diameter of 10 nm and very narrow diameter distribution is achieved. Also this ratio favors the yield of CNTs. The much larger ratio leads to the formation of many carbon fibers larger than 100 nm in diameter. And the much smaller ratio leads to the rapid deactivation of catalyst. The thermal stability and dispersion of nanometer iron crystalline is analyzed in detail. Also the influence of operating temperature (823-1023 K) on the yield and morphology of as-grown CNTs is also studied thoroughly. It is found that temperature lower than 873 K favors the catalytic decomposition of ethylene and hence the purity of CNTs. However, the high temperature leads to the serious thermal decomposition of ethylene and the production of amorphous carbon in large amount. Based on the above results, a diagram of the synthesis of small diameter distribution in high yield is determined, which is useful for the further investigation of the morphology of CNTs.

P9.20

PERMANENT DIPOLE OF CdSe NANORODS MEASURED BY TRANSIENT ELECTRIC BIREFRINGENCE. Liang-shi Li, A. Paul Alivisatos, Univ. of California, Berkeley, Department of Chemistry, Berkeley, CA.

The permanent dipole moment of nanocrystals has been an interesting subject. Besides the contribution from the arrangement of the atoms in the nanocrystals, the contribution from the surface trapped charges is also possible. The dielectric dispersion measurement on spherical wurtzite CdSe nanocrystals has shown that the dipole moment is from the surface charges, despite of the fact that they have non-centrosymmetric lattice structures. With transient electric birefringence we have measured the permanent dipole moment of CdSe nanorods with different lengths and widths dispersed in very dilute solution. The linear relationship between the longitudinal dipole moment with the nanocrystal volume suggests the non-centrosymmetric lattice of the nanocrystals indeed contribute to the dipole moment.

P9.21

SYNTHESIS OF CARBON MICRO-COILS AND NANO-COILS ON VARIOUS SUBSTRATES. Erik Einarsson, Jun Jiao, Logan Love, Portland State University, Dept of Physics, Portland, OR; Josie Prado, Oregon State University, Dept of Chemical Engineering, Corvallis, OR; George M. Coia, Portland State University, Dept of Chemistry, Portland, OR.

This research investigates the role of the substrate in the synthesis of carbon coils. Using electrochemically-deposited nickel (Ni) as a catalyst, the synthesis of carbon coils was attempted on tungsten (W), titanium (Ti), and glassy carbon via the chemical vapor deposition (CVD) of acetylene (C₂H₂) at 800°C. The W substrate consistently yielded carbon coils intermixed with thin carbon nanotubes, both

synthesized in high-yield. Carbon coils were also synthesized on the surface of Ti in small, high-yield patches, with few co-produced carbon nano-coils. Using glassy carbon as a substrate resulted in the synthesis of amorphous carbon, but no coil growth. Carbon coils were synthesized when pure Ni was used as both substrate and catalyst, indicating Ni itself is an important factor when synthesizing coils. Various results obtained when using different substrates implies the substrate also plays an important role. Potential applications of carbon coils as functional materials make the substrate on which they are synthesized important. Titanium is a strong material and is relatively inert, making it a good potential substrate for chemically sensitive environments. The same is true of glassy carbon, which is sometimes used in fuel cells. Tungsten is common to electron sources, making it a good substrate on which the field emission properties of carbon coils could be tested. All carbon coils synthesized were either micro-coils, which have a diameter of a few microns, or nano-coils, which have diameters of a few hundred nanometers.

P9.22

NEW CLASS OF SUPERCONDUCTING MULTILAYERS: SEMICONDUCTING MONOCHALCOGENIDE SUPERLATTICES. Yu. V. Bomze, O.I. Yuzepovich, A.I. Erenburg, B. Verkin, Inst. for Low Temp. Physics and Engineering, Kharkov, UKRAINE; A. Yu. Sipatov, Kharkov Polytechnic Institute, Kharkov, UKRAINE; V. Langer, Dept. of Inorganic Environm. Chemistry, Chalmers Univ. of Technology, Goteborg, SWEDEN; E.I. Buchstab, N. Ya. Fogel, Solid State Institute, Technion, ISRAEL.

It is possible to create composites whose elastic and conducting properties vary periodically on the nano-scale without the nano-technological means, if one deals with specific materials. This concerns, in particular, the superlattices (SL), consisting of the semiconducting NaCl-type cubic monochalcogenides of different metals, which have been grown epitaxially. The nano-scale in-plane modulation arises, which is due to appearance of regular grids of edge misfit dislocations (EMD) on the interfaces between two isomorphous compounds. The most remarkable property of multilayers studied is appearance of superconductivity at rather high temperature 2.5-6.4 K. The superconducting, electric and structural properties of SLs have been investigated. The main results are as follows: i) All SLs containing one or two narrow-gap semiconductors (PbS, PbSe, PbTe, SnTe) reveal superconducting transitions. Superconductivity is not discovered in combinations containing only wide-gap semiconductors (YbS/EuS, YbS/YbSe). ii) All superconducting SLs have metallic-type conductivity. iii) All superconducting samples are single crystals, which contain continuous EMD grids on the interfaces. When the dislocation grids do not cover the entire area of the interfaces the superconducting transition appears incomplete. iv) For the superconducting compositions there is a correlation between the values of the transition temperature T_c and the period of the misfit dislocation grid D . When interdislocation distance D diminishes the reduction of T_c is observed. Thus, many correlations between superconductivity appearance and the EMD grid existence are discovered. It is found that the systems studied consist of the superconducting layers located on the interfaces between two semiconductors separated by the non-superconducting material interlayers [1]. The interfaces are saturated with dislocations. We assume that in layered chalcogenides dislocation-induced superconductivity takes place, which is associated with inhomogeneous band inversion in narrow-gap semiconductors created by dislocation stress fields. 1. N.Ya.Fogel, E.I.Buchstab, Yu.V.Bomze, O.I. Yuzepovich, A.Yu. Sipatov, E.A. Pashitskii, A. Danilov, V. Langer, R.I. Shekhter, and M. Jonson, Phys. Rev. B 66, 2002.

P9.23

CHARACTERIZATION OF A SURFACE-ATTACHED ROTAXANE BY X-RAY ABSORPTION AND X-RAY PHOTOEMISSION SPECTROSCOPY. Andrew L. Vance, Trevor M. Willey, Tony van Buuren, A.J. Nelson, C. Bostedt, Louis J. Terminello, Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, CA.

Mechanically interlocking molecules are of interest for their potential in molecular-scale devices. X-ray absorption spectroscopy (XAS) and X-ray photoemission spectroscopy (XPS) were utilized to characterize a surface-attached rotaxane on a gold-coated substrate. Monolayers were prepared from an anthracene-stoppered thiol thread, a pseudorotaxane obtained by mixing the thiol with dibenzo-24-crown-8, and a disulfide-containing [3]rotaxane. XAS and XPS showed clear distinctions between the monolayers, allowing identification of spectral contributions from the separate components of the surface-attached rotaxane (surface-bound thiol stopper and mechanically-anchored crown ether ring). While both the pseudorotaxane and the [3]rotaxane could form surface-attached rotaxanes, the spectroscopic data clearly showed that only the [3]rotaxane gave the desired gold-bound interlocking molecule. These results highlight the importance of precursor design in the preparation of surface-attached interlocking

molecules. 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.

P9.24

A NEW CONCEPT OF VARIABLE CAPACITORS BASED ON CLUSTERS IN THE COULOMB BLOCKADE REGIME. P. Seneor, N. Lidgi, J. Carrey, F. Nguyen VanDau, H. Jaffrès, A. Fert, F. Petroff, A. Vaures, A. Friederich, Unite Mixte de Physique CNRS-THALES, Orsay, FRANCE.

Variable capacitors are widely used in radio-frequency applications. We propose a new concept of variable capacitor based on nanometric clusters in the Coulomb blockade regime. Those capacitors are constituted of two metallic electrodes separated by a thin (few nm) insulating layer in which a 2D array of nanometric metallic clusters is embedded. The Coulomb blockade phenomenon arises from the necessity to overcome the repulsing Coulomb energy when trying to add an electron from an electrode to an isolated cluster. This phenomenon is traduced in the first place by the existence of a threshold voltage (V_T) to add an electron to a cluster. If one adds a small AC voltage modulation to V_T , then during each cycle the particle will charge and discharge itself. This charge-discharge cycle creates a small AC current between the electrode and the cluster inducing a differential capacitance peak at V_T . When dealing with a large assembly of clusters, the overall capacitance variation versus voltage will strongly depend on their size distribution. We have developed a model that let us hope to control the voltage range and amplitude of the capacitance variation using an appropriate cluster distribution. Experimental evidence of the concept has been obtained on tunnel junctions including cobalt (2-4nm) clusters. We will present the model and the first experimental evidence of variable capacitors.

P9.25

STRUCTURAL EVOLUTION OF SELF-ASSEMBLED GERMANIUM ISLANDS ON SILICON (001) DURING HIGH GROWTH RATE LPCVD. G.D.M. Dillway and D.M. Bagnall, Univ of Southampton, Dept of Electronics and Computer Science, Southampton, UNITED KINGDOM; N.E.B. Cowern and C. Jeynes, Univ of Surrey, Advanced Technology Institute, Guildford, UNITED KINGDOM.

Understanding the process of self-organization of Ge nanostructures on Si with controlled size distribution is a key requirement for their practical applications. In this study, we investigate the temporal evolution of the structure of self-assembled islands during the low pressure chemical vapor deposition (LPCVD) of Ge on Si at 650°C using higher growth rates (6-9 nm/min) than previously reported. The islands were characterized by atomic force microscopy, transmission electron microscopy and Rutherford backscattering spectrometry. The first structures to assemble are small islands, ~4 nm high and 20 nm wide, with a narrow size distribution. These are typical of the lens-shaped structures reported in previous studies. Next to form is a population of larger islands with a broad height distribution, 4-25 nm (mean ~10 nm) and widths up to 150 nm. These islands have a lower aspect ratio (height/width) than the small ones, and appear different from the pyramid-shaped islands previously reported for this size range. We are investigating their microstructure further. Finally, the largest islands that form are square-based truncated pyramids with a very narrow size distribution, 50 nm high and 250 nm wide. Such pyramidal structures have previously been reported to occur at smaller sizes. Furthermore, we see no evidence of the multifaceted domes previously reported in this size range. The small lens-shaped islands appear to be defect-free, whilst some of the intermediate-sized islands and all the large truncated pyramids contain misfit dislocations. The difference between our results and previous observations is attributed to the higher growth rates we are using, which appear to delay the formation of lower energy structures during growth. Our study suggests that the use of high growth rates in LPCVD offers potential for a novel route to the fabrication of Ge nanostructures on Si with a more controlled structure and size distribution.

P9.26

TEMPERATURE DEPENDENT ESR OF DOPED CHALCOGENIDE NANOTUBES. Denis Arčon, Andrej Zorko, Pavel Cevc, Aleš Mrzel, Maja Remškar, Dragan Mihailovič, Institute Jožef Stefan, Ljubljana, SLOVENIA; Robert Dominko and Miran Gaberšček, National Chemistry Institute, Ljubljana, SLOVENIA.

Temperature dependence of the X-band ESR signal of the electrochemically doped self-assembled MoS₂ nanotubes [1] was measured between room temperature and 4 K. Two distinct ESR components were observed: a minor narrow component with a linewidth of about 4 G and a broad one with a linewidth of more than 800 G. The broad ESR component is attributed to the Li⁺ intercalation into the channels between the MoS₂ nanotubes and a

simultaneous electron charge transfer to the Mo *d*-state derived conducting band of MoS₂ nanotube. Large weakly temperature dependent ESR spin susceptibility of charged MoS₂ nanotubes may reflect their peculiar electronic structure including the presence of van Hove singularities in the density of states or correlation effects. During the intercalation process many different defects can be formed. These defects determine the low-temperature electronic properties of doped MoS₂ nanotubes and can ultimately even lead to Anderson-type charge localization. The narrow component is suggested to be due to the formation of small metallic Li particles during the doping process and may even reflect a dendritic growth of Li. [1] M. Remškar et al., *Science* **292**, 479 (2001).

P9.27

ATOMISTIC SIMULATION STUDY OF CONTROLLED NANOSTRUCTURE PATTERNING. B. Lee and K. Cho, Stanford University, Dept of Mechanical Engineering, Stanford, CA.

Quantum dots and nanoclusters have recently become an important research topic for applications to novel nanodevices. Many ways have been suggested to control the size and shape of the clusters so far, one of which is the self assembly due to the strain field generated from the mismatch between a substrate and a mismatched epitaxial layer on it. In this study, we will focus on the nanocluster kinetics with structures already discovered from the experiment as well as theoretical work using Embedded Atom Method (EAM). First principle calculations has successfully predicted that strain can affect the adatom kinetics and eventually guide the assembly of adatoms on the metal surface but it is almost impossible to use it to simulate a realistic system because of its very high computational cost. On the other hand, the conventional EAM model fitted only to the bulk experimental properties cannot predict the non-bulk kinetics, i.e. surface, clusters correctly. The new EAM proposed in this work is fitted to the bulk properties as well as cluster data obtained from the DFT calculations to overcome the limitations of the conventional EAM. The effect of the applied strain on surface adatoms as well as the interaction between adatoms will be investigated.

P9.28

FABRICATION AND GROWTH MECHANISM OF SELF-ASSEMBLED CARBON NANOTUBE FILM ON Ni/Mo NANOCOMPOSITE SUBSTRATE. Yoshiki Shimizu, Takeshi Sasaki, Tetsuya Kodaira, Kenji Kawaguchi, Naoto Koshizaki, Nanoarchitectonics Res Ctr, AIST Tsukuba Central 5, Ibaraki JAPAN; Kazuo Terashima, Grad Sch Frot Sci, The Univ of Tokyo, Tokyo, JAPAN.

We have prepared vertically aligned carbon nanotubes on various kinds of Ni-based substrates by the plasma assisted hot filament chemical vapor deposition. On Ni/Mo nanocomposite substrate in certain atomic ratio, cone-shaped carbon nanotube assemblies like cedar trees formed. These assemblies were distributed in a densely packed geometry on the substrate and it looked like a cedar tree forest. Based on the observation of the initial growth stages by scanning electron microscopy, transmission electron microscopy and Auger elemental mapping, we concluded the following formation mechanism of these assemblies. Droplet-like Ni, about 200 nm in diameter, initially forms on the substrate by thermally induced phase separation. Carbon nanotubes, 20 nm in diameter, grow from the droplet-like Ni by the well-known tip growth mechanism and form the cone-shaped assemblies. Later on, they grow more and merge together to form larger cone-shaped assemblies by further deposition. The relationship between the mean volume and the number density of conical-shaped tree-like assemblies corresponded to one of natural plant forest.

P9.29

SELF-ASSEMBLED ALTERNATING CARBON AND METALLIC LAYERS. Wan-Yu Wu, Jyh-Ming Ting, Department of Materials Science and Engineering, National Cheng Kung University, Tainan, TAIWAN.

In physical vapor deposition multi-layer thin films are normally obtained using co-sputtering techniques or more than one sputtering targets. In this paper we report the use of a dc sputter deposition system equipped with only one single magnetron gun to deposit self-assembled two-phase, multi-layer thin films. The target materials used include Pt, Cu, and Ni, while the reactive gas was Ar/CH₄. The self-assembled structures were accomplished through well-controlled deposition parameters and, more importantly, the selection of material systems. The key deposition parameters include pressure and dc power. The resulting multi-layer thin films consist of alternating layers of amorphous carbon and either platinum or copper. From the cross-sectional images obtained using high resolution transmission electron microscopy (HRTEM), it was found that the carbon layer is thicker than the metallic layer. The former has an average thickness of 20 nm, while the latter has an average thickness of less than 3 nm. In

a few cases, it was found that the carbon layer is in fact composed of a matrix of carbon with either platinum or copper nano-particles. The metallic layer, on the other hand, is pure metallic in any cases. When Ni was used as the target material, it was found that the combination of carbon and nickel did not lead to such multi-layer structure. It is noted that platinum is a noble metal, copper and carbon are immiscible, and nickel and carbon form carbide. Discussion is thus given concerning the carbon-metal interaction, which is thought to dominate the formation of the self-assembled multi-layer structure.

P9.30

INTERMIXING, STRUCTURAL AND ELECTRONIC PROPERTIES OF Au NANODOTS ON Si. Chin-Lung Kuo and Paulette Clancy, Cornell University, School of Chemical and Biomolecular Engineering, Ithaca, NY.

Metal nanodots self-assembled on silicon substrates show promise for novel memory devices and interconnects. Since the morphology, size, and spacing of metal nanodots and the properties of the interface region can affect the quality of the devices, understanding how the processing conditions influence the formation of metal nanodots on Si substrates and influence the properties of the interface is an important issue for device fabrication. Although experimental recipes for nanodot formation are available, a fundamental understanding of the factors affecting nanocrystal formation is still fragmentary. The purpose of this study is to apply molecular simulation techniques to investigate the formation of metal nanodots on a semiconductor substrate, here Au nanodots on Si(100). Molecular Dynamics combined with Modified Embedded Atom Method (MEAM) models is used to examine the properties of the Au/Si system. Development of appropriate Au-Au and Au-Si MEAM potential functions are presented. For the Si-Si interactions, we employ the MEAM potentials developed previously (Baskes, 1992). The simulations showed that gold and silicon intermix readily in the interfacial region and that the formation of silicides is very fast. Silicides can be formed at very low coverage (~0.11 ML) and in the very early stages of the simulation (~1.0 ps). After about 1ML deposition, the intermixing layer reached saturation, i.e. further deposition of Au does not significantly change the thickness of the intermixed region. There is a structural transition from disordered silicides at low coverage (< 1 ML) to a crystalline Au top layer as the number of monolayers is increased. The nature of the electronic structure in the interfacial region is presented. The influence of initial layer thickness and RTA profiles on the size distribution of the Au nanodots will also be discussed.

P9.31

ELECTROCHROMIC PROPERTIES OF WO_x THIN FILMS FORMED BY LASER ASSISTED MOLECULAR BEAM DEPOSITION (LAMBD). P.V. Ashrit, Thin Films and Photonics Research Group, Department of Physics and Astronomy, Universite de Moncton, Moncton, NB, CANADA; Robert L. DeLeon, James F. Garvey, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY; G.S.Tompa, AMBP Tech Corp, Amherst, NY.

The phenomenon of electrochromism (EC), in which a reversible optical property change can be induced in certain materials such as tungsten trioxide(WO₃) films, has become increasingly important from an application point of view. Recent studies have shown that a well tailored nanostructure in these films can lead to high efficiency EC coloration in various spectral regions of interest. The novel technique of Laser Beam Assisted Molecular Beam Deposition (LAMBD) has been employed in this work to achieve high optical quality tungsten oxide thin films. This technique of film deposition is based on ablating the required tungsten metal target by a pulsed laser and using a train of oxygen gas pulses to precisely control the chemistry and transport of the formed tungsten oxide species onto the substrate. The effect of various deposition parameters on the optical and electrochromic properties has been studied in detail, especially, with the aim of achieving highly transparent nanostructured films. The films have been characterized by reflection/transmission ellipsometry, atomic force microscopy (AFM), XRD and spectrophotometry both in the normal (clear) state and under Li intercalated (colored) state. The application potential of the LAMBD technique to achieve the required precise nanostructure is evaluated.

P9.32

SELECTIVE SURFACE MIGRATION FOR DEFECT-FREE QUANTUM DOT ENSEMBLES USING METAL ORGANIC CHEMICAL VAPOR DEPOSITION. S. Birudavolu, A.A. El-Emawy, P.S. Wong, S. Huang, H. Xu, Y. Xin and D.L. Huffaker, Center for High Technology Materials, University of New Mexico, Albuquerque, NM.

In this presentation, we discuss a growth technique that allows significant reduction of quantum dot (QD) coalescence without altering the QD density. This technique allows the first demonstration of 1.3 micron electroluminescence from a MOCVD-grown ensemble.

Although the first In(Ga)As QDs emitting at 1.3 micron under photo-excitation were grown using MOCVD in 1994[1], there have been relatively few reports([2],[3],[4]) of 1.3 micron to 1.5 micron emission from MOCVD-grown QDs and the 1.3 micron QD laser grown using MOCVD has not yet been demonstrated. Shorter wavelength MOCVD-grown QD lasers demonstrate low threshold and high output power([5],[6]). However, increasing the wavelength of MOCVD-grown QDs has been difficult due to the increased density of coalesced QDs that form with increased strain and complicated surface environment at low growth temperatures(500 C)[7]. In our study, we balance the nucleation rate and adatom surface migration using an AsH₃ pause just after QD deposition. Pausing the AsH₃ flow for a few seconds allows surface atoms to migrate from poly-crystalline defect sites where the bond strengths are weak to crystalline QD sites. This selective migration allows the reduction of defects density from 1.9 x 10⁹/cm² (0 sec AsH₃ pause) to a defect-free QD ensemble (60 sec AsH₃ pause) without significantly changing the QD density. We will discuss statistical analysis based on atomic force microscope images, high-resolution transmission electron microscopy, photoluminescence and electroluminescence to characterize the effects of AsH₃ pauses on the QD density and crystallographic shape. We will also discuss device characteristics from QD lasers grown using this technique. References: [1]K. Mukai, N. Ohtsuka, M. Sugawara, S. Yamazaki, J. J. Appl. Phys., Part 2 (Letters), 33, L1710 (1994). [2]J. Tatebayashi, M. Nishioka, Y. Arakawa, Appl. Phys. Lett. 78, 3469 (2001). [3]N.N. Ledentsov, M.V. Maximov, D. Bimberg, T. Maka, C.M. Sotomayor Torres, I.V. Kochnev, L.L. Krestnikov, V.M. Lantratov, N.A. Cherkashin, Yu.M. Musikhin, Semiconductor Science and Technology 15, 604 (2000). [4]A. Passaseo, G. Maruccio, M. De Vittorio, R. Rinaldi, R. Cingolani, M. Lomascolo, Appl. Phys. Lett. 78, 1382 (2001). [5]F. Heinrichsdorff, A. Krost, D. Bimberg, A.O. Kosogov, P. Werner, J. Appl. Phys. Part 1 (Regular Papers, Short Notes & Review Papers) 36, 4129 (1997). [6] R.L. Sellin, Ch. Ribbat, M. Grundmann, N.N. Ledentsov, D. Bimberg, Appl. Phys. Lett. 78, 1207 (2001). [7]F. Heinrichsdorff, A. Krost, M. Grundmann, D. Bimberg, F. Bertram, J. Christen, A. Kosogov, P. Werner, J. Cryst. Growth, 170, 568 (1997).

P9.33

EPITAXIAL CONSTRAINTS ON THE CONTACT FACETS OF Ge QUANTUM DOTS ON Si(100). Eli Sutter, Peter Sutter, Percy Zahl, Department of Physics, Colorado School of Mines, Golden, CO.

Epitaxial quantum dot islands, formed by strain-induced self-assembly, have attracted much interest recently. In view of potential applications in electronics, detailed knowledge of the shape of these quantum dots is important. In the most common model system, Ge/Si(100), an intriguing sequence of shape transformations has been identified, and explained in terms of the progression of strain relaxation. At the initial stage of three-dimensional (3D) growth, shallow {105} faceted pyramids form, which later transform into a multifaceted dome shape. Using a combination of in-situ scanning tunneling microscopy and cross-sectional transmission electron microscopy, we observe that even long after the pyramid-dome shape transition, {105} facets persist at the island base. This leads to a small (~11°) contact angle of the domes with the Si(100) substrate. We demonstrate that a {105} faceted base is a consequence of the pyramid-dome transition, and - stabilized by lattice mismatch strain - is part of the epitaxially constrained equilibrium shape of the domes. Our results indicate an unexpectedly complex interplay between geometric relaxation in the island and induced strain fields in the substrate in determining the epitaxially constrained island shape.

P9.34

THE FORMATION OF QUASI-ONE-DIMENSIONAL Cu₂O STRUCTURES BY IN-SITU OXIDATION OF Cu(100). Guangwen Zhou and Judith C. Yang, Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA.

In the rapidly developing field of nanotechnology, formation of self-assembled islands through surface processes has been intensively investigated because of potential applications and the intrinsic interest in structure with reduced dimension. One intriguing aspect in these self-assembled systems is the tendency of the islands to change their shape as they increase in size. We report the first observations of a surface chemical reaction where the nanorod transition is observed. Epitaxial Cu₂O islands on Cu(100) surface formed through oxidizing Cu(100) films at 600°C in an ultra-high vacuum transmission electron microscope (UHV-TEM) were observed to undergo a shape transition from initially square shaped islands to elongated islands at a critical size of ~110nm. The islands grew anisotropically in the {001} directions of Cu(100) surface. We have observed such elongated islands with aspect ratios as large as 40:1. Our experimental data on the elongation of Cu₂O islands agree with the energetic calculations based on the balance between surface and interface energies and the elastic stress relaxation in the three dimensional islands. We developed a kinetic model based on oxygen surface diffusion that fits well with the observed volume evolution of the Cu₂O islands. The

oxide volume increases parabolically with respect to oxidation time before the shape transition, and exponentially after a few minutes beyond the shape transition.

P9.35

PHOTOCATALYTIC DECOMPOSITION OF ALKYL-SILOXANE SELF-ASSEMBLED MONOLAYERS. Myung M. Sung, Chan R. Park, Hyon T. Kwak, Kookmin Univ, Dept of Chemistry, Seoul, KOREA.

The photocatalytic decomposition of octadecyltrichlorosilane(OTS) based self-assembled monolayer formed on TiO₂ has been studied using atomic force microscopy(AFM), x-ray photoelectron spectroscopy(XPS) and contact angle analysis. Densely-packed alkylsiloxane monolayers similar in quality to those on SiO₂ are formed on TiO₂. It is found that the monolayers on TiO₂ decompose much faster than those on SiO₂ under UV illumination in air. The observation indicates that the titanium oxide, a well-known photocatalyst for organic pollutant treatment, efficiently decompose the alkylsiloxane monolayers under UV illumination in air. The bottom-up fabrication techniques based on TiO₂ and SAMs will be discussed which might be applied to the fabrication of microelectronic and other complex molecular-scale devices.

P9.36

OPTIMIZATION OF INDIUM GALLIUM ARSENIDE FILMS FOR SELECTIVE EPITAXY OF InAs QUANTUM DOTS. T.S. Yeoh and A. Gaur, Dept. of Materials Science and Engineering, University of Illinois, Urbana, IL; R.B. Swint, V.C. Elarde, and J.J. Coleman, Dept. of Electrical and Computer Engineering, University of Illinois, Urbana, IL.

Quantum dot selective epitaxy by indium segregation is an alternative to oxide-masked selective area epitaxy. This method achieves selective growth by altering the additional coverage necessary to induce self-assembly, allowing uniform selectivity over the entire wafer. Experiments have been conducted to characterize the behavior of InGaAs film surfaces for optimal growth selectivity. The effects of pre-growth annealing temperature and film composition on selective growth of InAs quantum dots are reported. The optimal regrowth conditions appears to be a compromise between surface smoothing, strain-induced indium segregation, and temperature-induced indium desorption. As a result we report the epitaxy of defect-free InAs quantum dots selectively grown on GaAs using InGaAs thin films.

P9.37

EQUILIBRIUM SHAPES AS A FUNCTION OF SIZE AT THE Si(111) PHASE TRANSITION. G.E. Thayer, J.B. Hannon, R.M. Tromp, IBM T.J. Watson Research Center, Yorktown Heights, NY.

The need for new techniques for nanoscale fabrication has driven renewed interest in self organization and self assembly at surfaces. On the Si(111) surface, it has been shown that temperature can be used to tune the size of 7x7 domains during a surface phase transition at T=1130K and that for a range of temperatures, these domains are stable with well defined equilibrium sizes and nearly no size distribution. This thermodynamic size selection of periodic arrays of triangular domains of the 7x7 surface phase is due to a balance of fundamental forces particular to surfaces and can be directly linked to surface stress and elastic relaxation at phase boundaries. Our current combined experimental and analytical investigation shows that it is not only the size of 7x7 domains that is determined by elastic relaxations on the surface but also the shape. We observe that for domain sizes of equilateral triangle length L=1µm the sides of the triangle bend inward toward the center of the triangular domain, while for L=0.2µm the sides of the triangle bend outward. This shape dependence on size of the 7x7 domain cannot be explained solely using the standard Wulff construction but can be described by taking surface stress into account. By an experimental and theoretical analysis of the magnitude of the bend as a function of domain size, we quantitatively measure the formation energy of the observed domain shape thus making a direct connection between surface stress and structure. Analytical theory shows that the nucleation, formation energy, shape and size selection of isolated domains due to a balance of fundamental forces such as elasticity and orientational dependence of the boundary energy can be described in terms of a small number of measurable parameters. Knowledge of these parameters in strain mediated self assembly systems is required for a detailed understanding and control of size and shape selection at surfaces.

P9.38

OPTIMIZATION OF THE INTERPLAY OF WEAK INTERACTIONS AND FUNCTIONAL GROUPS AT THE INTERFACE TO DESIGN DEFECT FREE NANOSTRUCTURED MATERIALS. Ling Guan Wong, Boon Tee Ong, Lakshminarayanan Rajamani, Jagadesan Subbiah, National University of Singapore, SINGAPORE.

Weak intermolecular interactions such as hydrogen bonds, van der Waal's forces play an important role in controlling the self-assembly of molecular building blocks. We are interested in exploring the structure-property-function triad of materials formed through self-assembly of small multifunctional molecules. The talk will focus on the design, characterization and property of the self-assembled architectures from both organic and inorganic building blocks in the solid lattice.

P9.39

Abstract Withdrawn.

P9.40

MODELING STABILITY OF TRAPPED COLLOIDAL FERROMAGNETIC NANOPARTICLE CHAINS. O.Hovorka, B. Yellen, and G. Friedman, Drexel University, Electrical and Computer Engineering Department, Philadelphia, PA.

Magnetic field directed assembly of superparamagnetic colloidal beads onto arrays of ferromagnetic traps has been investigated both theoretically and experimentally in several prior publications [1,2]. In contrast with other colloidal self-assembly approaches, magnetically driven assembly offers the potential for trapping colloidal beads only in selectively programmed locations on the surface, while repelling them from other locations. The main limitation of this technique, however, is that the magnetic moments in superparamagnetic beads smaller than 100 nm in diameter are too weak to effectively direct assembly. Ferromagnetic particles, on the other hand, have significantly larger magnetic moments and would be an excellent replacement if one could find ways to control their tendency to aggregate.

In this work, we present results from numerical models, which demonstrate the potential for controlling the aggregation of ferromagnetic nanoparticles near ferromagnetic traps. This analysis considers a nanopore that is partially filled with magnetic material and used to attract a chain of ferromagnetic nanoparticles to its surface. Once a chain is captured inside the nanopore, application of uniform magnetic field perpendicular to the pore axis causes the magnetization of the nanoparticles to rotate. It will be shown that above some critical field strength, the particles will repel one another, which causes the chain to break, leaving behind a single particle in the pore. The key difference in the use of ferromagnetic versus superparamagnetic particles is that the assembly process is highly dependent on field history. We take this history dependence into account with the classical Stoner-Wohlfarth model of particle magnetization reversal and by accumulating the history through the process of time-stepping.

1. B. Yellen, G. Friedman, A. Feinerman, J. Appl. Phys. 91, 8552 (2002).
2. B. Yellen, G. Friedman, European Cells and Materials, 3, 88 (2002).

P9.41

MODELING OF THE EVOLUTION OF NANOSCALE RING STRUCTURE ON THIN FILMS. Anter El-Azab and Don Baer, Fundamental Science Directorate, Pacific Northwest National Laboratory, Richland, WA; Yong Liang, Motorola Labs, Tempe, AZ.

We present a model for the morphological instabilities leading to the formation of nanoscale ring structure on thin films at high temperature, where both surface diffusion and evaporation are operative. The model is based on the mechanisms of deformation-diffusion instabilities, and aims at predicting the surface morphology based on coupled stress and surface diffusion fields. The strain field in a thin film with a perturbed surface, finite thickness, and elastic properties that are different from those of the underlying substrate has been developed analytically. This solution is used to derive the expression of the chemical potential on the film surface, the gradient of which defines the diffusive flux. A mass balance including both diffusion and evaporation is established, which gives the rate of the film surface motion. The ring morphology is found from the stability analysis of the system of equations, subject to axially symmetric bifurcation conditions, e.g., initial surface morphology or strain sources in the system. In addition to this linear stability analysis, the governing equations are solved for the time evolution of the surface. It is found that evaporation and substrate exposure and the film thickness play important roles in the stability of the evolving ring morphology and its transition to nano dot structure. Good agreement has been found between the model results and experimental images of recently observed nanoscale ring structure on the surface of a thin copper film processed at high-temperature in oxygen plasma.

P9.42

SELF-ASSEMBLED PARTICLES IN 2D. A. Ghazali, Groupe de Physique des Solides, UMR7588-CNRS, Universit s Paris 6 et Paris 7, FRANCE; J.-C.S. L vy, Laboratoire de Physique de la Mati re Condens e, Universit  Paris 7, FRANCE.

A self-assembling of nanometric particles interacting via a short-range potential well is obtained by means of Monte Carlo simulations at different temperatures and exhibits a number of quasi-equilibrium structures. At low temperature, the bonds between neighboring particles are strong enough and cannot be broken. So, the self-assembling is dominated by the particle diffusion and leads to a diffusion-limited aggregation (DLA) [1] with very thin branches. At moderate temperature, these bonds are softened by thermal fluctuations and particles can move. This results in a dendritic morphology akin to DLA shapes but with a few-grain branch thickness. At higher temperatures, this relaxation is enhanced and leads to the formation of compact islands, while a few stable individual particles are spread all over the sample. It is noteworthy that these arrangements correspond to the lowest average energies per particle. A further increase of the temperature leads to a gradual breaking of islands in smaller ones and in individual particles in a kind of 2D-melting or 2D-solid-gas transformation which proved to be a first-order transition. There are experimental observations of atomic organization in DLA-type fractal clusters, dendrites or compact islands of surface-supported deposits according to the deposition temperature [2], and also observations of different morphologies in supported islands made up of atom clusters [3]. A comparison of these observations with our simulation results will be given.

[1] T.A. Witten and L.M. Sander, Phys. Rev. B **27**, 5686 (1983).

[2] Harald Brune, Surf. Sci. Rep. **31**, 121 (1998).

[3] B. Yoon *et al.*, Surf. Sci. **443**, 76 (1999).

P9.43

CHARACTERIZATION OF ZnO NANORODS ASSEMBLED FROM NANODOTS. Richard D. Yang, Hung-Jue Sue, Polymer Technology Center, Dept. Mech. Eng., Texas A&M University, College Station, TX.

ZnO has remarkable optoelectronic properties that will have great potential applications in blue and UV light emitters. Semiconductor nanorods are reported to possess linearly polarized emission, high quantum efficiency and low lasing threshold properties. Thus ZnO nanorods will be a very good candidate for linearly polarized laser because of its high exciton binding energy (~60 meV) and shape effect. In this paper, ZnO nanorods are synthesized in a wet chemical routine assembled from nanodots. Absorption and fluorescence spectroscopy study have been carried out to study the assembly process. It has been found a shape absorption shoulder emerged at 350 nm during rods formation, which can be taken as the characteristic absorption peak of nanorods. Two emission peaks at 375 nm and 545 nm were found from fluorescence spectrum of 30 nm by 1000 nm nanorods. Different diameter (10-30 nm) and length (100 -1000 nm) nanorods were prepared and studied under high resolution TEM to correlate structure, size, shape and optical properties relationships. Other optical characterization techniques such as micro-Raman, micro-PL and time resolved PL would be carried out to further understand novel properties in ZnO nanorods. The growth mechanism of nanorods formation will be explained from the morphology and optical study as well.

P9.44

PERCOLATION AND ELECTRICAL CONDUCTIVITY IN ASSEMBLIES OF METAL NANOPARTICLES LINKED BY ORGANIC MOLECULES. K.-H. Muller, G. Wei, J. Herrmann, L. Wiczorek, B. Raguse, CSIRO, Telecommunications and Industrial Physics, Sydney, AUSTRALIA.

We have investigated theoretically and experimentally the electrical conductivity of films assembled from Au nanoparticles linked by alkane dithiol molecules. Conduction in these films is due to tunneling of single electrons between neighbouring metal nanoparticles via the linker molecules. During tunnelling electrons have to overcome the Coulomb charging energy. We find that the observed temperature dependence of the conductivity is non-Arrhenius like and can be described in terms of a percolation theory which takes account of disorder in the assembly. Disorder is caused by variations in the nanoparticle size, fluctuations in the separation gaps between adjacent nanoparticles and by offset charges. To explain in detail our experimental data, a wide distribution of separation gaps and charging energies has to be assumed [1]. We find that a wide Coulomb charging energy distribution can arise from random offset charges even if the nanoparticle size distribution is narrow. We demonstrate that the expected exponential decrease of the conductivity with increasing length of linker molecules is weakened by the presence of high conductance percolation pathways and that due to 3D current percolation the conductivity becomes film thickness dependent. In addition, we explain theoretically the observed nonlinear I-V characteristics of disordered Au nanoparticle films at different temperatures. [1] K.-H. Muller, J. Herrmann, B. Raguse, G. Baxter, and T. Reda, Phys. Rev. B **66**, 075417 (2002).

P9.45

THE PREPARATION OF LARGE SCALE SELF-ASSEMBLED MONOLAYER ARRAYS OF GOLD NANOPARTICLES ON MODIFIED SILICON SUBSTRATES USING A CONTROLLED PULLING METHOD. Richard D. Tilley, Satoshi Saito and Isao Matsui, Advanced Materials Laboratory, Toshiba Corporate Research & Development Center, Kawasaki, JAPAN.

Much of the recent interest in nanoparticles has been driven by their possible use in the next generation of information storage media, because they offer the possibilities of terabit-per-square-inch recording densities. For this potential to be fully utilized it is vital that a monolayer of nanoparticles can be assembled in an ordered array over a 2.5 inch disk with minimal bilayers or vacant areas. Gold nanoparticles with average sizes ranging from 3 - 10 nm were synthesized in reverse micro-emulsions using the surfactant cetyltrimethylammonium bromide (CTAB). Dodecanethiol was then attached to the surface of the particles, which were subsequently purified by liquid phase extraction. The formation of nanoparticle monolayer arrays was accomplished by vertically pulling various modified silicon substrates at controlled speeds from nanoparticle solutions. The silicon substrates used were 1 cm² in size and had silanol and hydrogen terminated surfaces, and surfaces chemically modified by (CH₃)₃SiNHSi(CH₃)₃ and (CH₃O)₃Si(CH₂)₂(CF₂)₇CF₃. The effect of the substrate pulling speed and solvent were also investigated. The results, assessed using atomic force microscopy (AFM), indicated that the surface modification was the most significant factor. Silanol terminated silicon substrates were found to have very low coverage and the carbon fluoride modified silicon substrates very high monolayer coverage. It was also found that lowering the substrate pulling speed and using higher boiling point solvents favored monolayer formation and by optimizing these factors a 95% monolayer coverage on the carbon fluoride modified substrate has been achieved. It is planned to extend the methods of these experiments to magnetic FePt nanoparticles capped with groups containing alkane chains. Conclusions about the mechanism of monolayer formation will also be presented.

P9.46

INVESTIGATION OF COPPER(I) OXIDE QUANTUM DOTS BY NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE AND X-RAY PHOTOELECTRON SPECTROSCOPY. P. Nachimuthu and D.W. Lindle, University of Nevada, Department of Chemistry, Las Vegas, NV; S Thevuthasan, A.S. Lea, M.H. Engelhard, D.R. Baer, Pacific Northwest National Laboratory, Richland, WA; D.K. Shuh, R.C.C. Perera, Lawrence Berkeley National Laboratory, Berkeley, CA; Y.J. Kim, Hanbat National University, Department of Chemical Technology, Taejeon, KOREA.

Copper oxide quantum dots (CuOQD) were grown in various thicknesses on different SrTiO₃(001) surfaces and were investigated by near edge x-ray absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS). The experimental growth conditions for the CuOQD were optimized to obtain Cu₂O as the major phase. The CuOQD grown on clean SrTiO₃(001) surfaces at 825 K or higher with p(O₂) of 9.0x10⁻⁷ Torr or above contain mostly CuO contrasting to CuOQD grown at 800 K with p(O₂) of ~7.0x10⁻⁷ Torr that contain primarily Cu₂O. Furthermore, it is established that there is a strong interaction between the SrTiO₃(001) surface and the first few monolayers of the CuOQD, which induces the formation of Cu(II). However, this interaction is mitigated with increasing thickness of CuOQD resulting in the exclusive formation of Cu₂O in the topmost layers. The influence of the SrTiO₃(001) substrate on the formation of CuOQD can be reduced by modifying the substrate surface using chemical treatment and/or energetic Au²⁺ ion-beam irradiation, since the substrate effect results from the reaction between the substrate oxygen and the copper atoms from the CuOQD. Examination of the photochemical properties of these CuOQD shows that prolonged soft x-ray irradiation under vacuum reduces Cu(II), which is present as a minor impurity in the CuOQD.

P9.47

INFLUENCE OF CAPPING GROUPS ON THE SYNTHESIS OF MAGNETIC NANOPARTICLES. Ming Yin and Stephen O'Brien, Columbia University, Dept of Applied Physics and Applied Mathematics; Amanda Wills, Dept of Chemistry, New York, NY.

Monodispersed and uniform γ -Fe₂O₃ maghemite nanoparticles were prepared by thermal decomposition of iron pentacarbonyl in the presence of capping group and the following controlled oxidation by using trimethylamine oxide as a mild oxidant. A variety of capping groups-carboxylic acid with different carbon chain lengths (octanoic acid, lauric acid and oleic acid), and with different carbon chain structures (trans-oleic acid and cis-oleic acid) were used to study the synthesis of γ -Fe₂O₃ nanoparticles. The effect of the molar ratios of surfactant to iron precursor were also studied by using oleic acid as the capping group. The nanoparticles were characterized by nuclear

magnetic resonance, infrared spectra, x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD showed the particles were highly crystalline structure at nanometer scale. TEM showed well self-assemblies of monodispersed nanoparticles with different size and distances between each other. The results showed that the size and shape of the nanoparticle is strongly influenced by decomposition temperature of iron pentacarbonyl, which is closely related to the length of carbon chain of the capping groups and the molar ratio of surfactant to iron precursor. The longer the carbon chain, the higher the decomposition temperature, and higher ratio of surfactant to iron precursor reduced the decomposition temperature of iron pentacarbonyl. It is also found that in a self-assembly structure, the distance between the nanoparticles matched the length of capping molecules very well.

P9.48

NANOPARTICLE-MEDIATED COLLOIDAL ASSEMBLY.

Angel T. Chan, Carlos J. Martinez, and Jennifer A. Lewis, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL.

Binary mixtures consisting of attractive colloidal microspheres and strongly repulsive nanoparticles exhibit rich behavior driven by both energetic and entropic effects. In such systems, we have recently observed a new colloidal stabilization mechanism, known as nanoparticle haloing. Here, we report on the generality of our discovery through studies of a model binary mixture of colloidal silica and fluorescently labeled polystyrene nanoparticles. Confocal microscopy in combination with ellipsometry, zeta potential measurements and other characterization techniques, have been used to investigate their phase behavior and structure as a function of composition, pH and ionic strength.

P9.49

NANOSTRUCTURE OF SURFACE FORMED BY VACANCY CLUSTERING IN FeAl. Kyosuke Yoshimi and Tomohide Haraguchi,

Tohoku Univ., Center for Interdisciplinary Research, Sendai, JAPAN; Tomohisa Ogawa, Tohoku Univ., Dept. of Biomolecular Science, Sendai, JAPAN; Takayuki Kobayashi, Min-Seok Sung, Shuji Hanada, Tohoku Univ., Institute for Materials Research, Sendai, JAPAN.

It is well established that the surface of metals and alloys behaves as a sink and source for vacancies in bulk. In B2-type FeAl, supersaturated vacancies retained upon rapid quenching are absorbed near surface during an aging treatment, being agglomerated into nano to mesoclusters through the absorption process. Eventually, surface structure is self-patterned in nano-order by the vacancy clustering. If FeAl is not quenched from high temperature or plastic strain is left near the surface, the self-patterning never occurs, indicating that the change in surface structure is due to the vacancy clustering. The clusters have specific morphology and crystallography with cluster surfaces faceting toward {100} planes. Thus, the shape of the clusters formed near surfaces is controllable by changing surface orientation; e.g., rectangular for the {100} plane, triangular for the {111} plane and gutter-like for the {110} plane. Cluster size and distribution density can be also controlled by varying the concentration of supersaturated vacancies and/or the clustering treatment. For instance, with increasing quenching temperature, the concentration of the vacancies is increased, and then the cluster size becomes smaller and the distribution density higher. These obtained results indicate that the vacancy clustering is a unique process which enables us to efficiently pattern the surfaces of metals, alloys and intermetallics in nano-order.

P9.50

EFFECTS OF LATERALLY AND VERTICALLY NEIGHBORING QUANTUM DOTS ON FORMATION OF A NEW SURFACE QUANTUM DOT. Bo Yang and Vinod K. Tewary, Materials

Reliability Division, National Institute of Standards and Technology, Boulder, CO.

We examine the driving force for formation of a surface quantum dot (QD) near laterally and vertically neighboring seed QDs in a linear anisotropic elastic substrate. The driving force is parameterized by the elastic energy release rate (EERR), defined as relaxation energy per unit volume of quantum dot growth. An efficient boundary-element method is used to solve the three-dimensional multiple-body problem of anisotropic elasticity, which requires numerical discretization only along the surfaces of the QDs and their interfaces with the substrate. Numerical results are reported for InAs QDs of cuboidal shapes on a GaAs substrate with a free surface along the (001) plane. By assuming that the spatial variation of the total change of free energy (including elastic energy, surface energy and edge energy) depends only upon the elastic-energy part, the favorable location and driving force for formation of a new surface QD in the presence of a seed QD are determined. It is found that the presence of a surface seed QD inhibits the growth of a new surface QD. The new QD prefers to align

with the seed QD in the (100) and (010) directions. In contrast, in the presence of a buried seed QD, the driving force for the growth of a new QD at the favorable location is enhanced. In addition, the theory predicts an optimum depth of the buried seed QD for the driving force for the growth of a new QD at the surface.

P9.51

1.3 μ InAs/GaAs QUANTUM DOTS DIRECTLY CAPPED WITH GaAs GROWN BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION. Nien-Tze Yeh and Wen-Jen Ho, Telecommunication Laboratories, Chungwa Telecom Co., Ltd., Yang-Mei, TAIWAN; Kun-Fu Huang and Meng-Chyi Wu, National Tsing Hua Univ, Dept of Electrical Engineering, Hsin-Chu, TAIWAN; Ton-Po Shieh and Jen-Inn Chyi, National Central Univ, Dept of Electrical Engineering, Chung-Li, TAIWAN.

Self-organized quantum dots (QDs) heterostructures on a GaAs substrate have been shown to achieve 1.3 μ m emission. One is grown defect-free InGaAs quantum dots on GaAs surface. One alternative way is InAs quantum dots covered with a InGaAs strain reducing layer (SRL) or placed in the middle of InGaAs quantum well. In this work, we study the growth of 1.3 μ m InAs quantum dots directly capped by GaAs layer without InGaAs SRL. All samples were grown by metal organic chemical vapor deposition (MOCVD) on (100) 2 degree off (111)A Si-doped GaAs substrate and have been deposited using trimethylindium (TMIn), trimethylgallium (TMGa) in combination with arsine (AsH₃). The growth temperature is 650°C for the GaAs buffer, 480-560°C for InAs QDs and 500°C for the GaAs cap layer. The InAs QDs were grown with interruptions corresponding to 0.3 monolayer of InAs and 15 seconds of AsH₃ irradiation for each period. We have observed the peak wavelength and intensity of PL spectra for InAs QDs at the deposition temperature from 480 to 560°C. The relationship could be divided into two zones. The intensity and wavelength of PL increase when temperature is below 500°C, and the intensity and wavelength of PL decrease when temperature is above 500°C. Then the optimum growth temperature in our growth system for 1.3 μ m InAs QD is 500°C. In this optimum growth temperature, we find that the emitting wavelength of InAs QDs directly capped with GaAs can be extended to 1.33 μ m with narrow PL linewidth of about 30 meV. The corresponding scanning electron microscopy image shows a very large size of InAs QDs with diameter of 45 nm and density of $7 \times 10^9/\text{cm}^2$. Thus the extension of PL peak could be attributed the enlargement of the size of InAs QDs.

P9.52

EARLY STAGES OF SELF-ASSEMBLED NANOWIRE FORMATION DURING CU DEPOSITION ONTO VSe₂ CRYSTALS. Stefan Hollensteiner, Erdmann Spiecker, Wolfgang Jäger, University of Kiel, Faculty of Engineering, Kiel, GERMANY; Herbert Schroeder, H. Haselier, Institute for Solid State Research, Research Center Jülich, Jülich, GERMANY.

Self-assembled metallic nanostructures gain increasing interest in nanotechnology owing to their potential application in future electronic devices. Recently it has been shown that self-assembled nanowire networks can be produced by deposition of Cu onto atomically flat surfaces of VSe₂ crystals^{1,2}. While the arrangement of the nanowires has been studied in some detail for moderate and high Cu coverages there is little knowledge about the early stages of the wire formation. Samples with nominal Cu coverages between 4 Å and 25 Å have been prepared by UHV electron beam evaporation at room temperature onto freshly cleaved VSe₂ crystals. Scanning transmission electron microscopy and various methods of analytical transmission electron microscopy including electron diffraction studies, Moire pattern imaging and energy dispersive X-ray microanalysis have been applied to the investigation of the arrangement and the structure of the nanowires. At the lowest coverage of 4 Å a few large wires with lateral dimensions of about 150nm are observed pointing to a pronounced surface diffusion of the deposited Cu atoms. At coverages of 10 Å and above a uniform network of nanowires of smaller lateral dimension (~20nm - 40nm) with partly hexagonal and partly square meshes develops on substrate terraces in addition to the large wires. Nanowires of both dimensions are characterized by a separation into two wire strands composed of crystalline grains which show nearly epitaxial relationships with respect to the substrate. The temporal evolution, the preference of certain wire directions, and the grain-substrate orientation relationship will be discussed with regard to the nanowire formation mechanism.

¹R. Adelung, F. Ernst, A. Scott, M. Tabib-Azar, L. Kipp, M. Skibowski, S. Hollensteiner, E. Spiecker, W. Jäger, S. Gunst, A. Klein, W. Jägermann, V. Zaporozhtchenko, F. Faupel, Adv. Mat. 14 (2002), 1056. ²S. Hollensteiner, E. Spiecker, C. Dieker, W. Jäger, R. Adelung, L. Kipp, M. Skibowski, Mat. Sci. Eng. C (in press).

P9.53

PHOTOLUMINESCENT PROPERTIES OF HIGH QUALITY ZnO SINGLE-CRYSTAL NANORODS GROWN BY CATALYST-FREE

METALORGANIC VAPOR PHASE EPITAXY. Won Il Park, Gyu-Chul Yi, Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang, KOREA.

One-dimensional semiconductor nanowires and nanorods are potentially ideal functional components for nanometer-scale electronics and optoelectronics. Homogeneous and heterostructural nanowires have already been employed in various nanoscale devices. However, the ability to reduce defect concentrations in the semiconductor nanomaterials is required for many new device applications, as already proven in thin film semiconductor electronics and photonics. In particular, high purity single crystalline materials are essential to be prepared because an extremely small amount of unintentionally incorporated impurities is known to significantly affect electrical and optical properties of semiconductors. Here, we present observation of free excitonic emission peaks from photoluminescence spectra of ZnO single crystal nanorods at 10 K resulting from their low defect concentration. Low temperature PL spectra measured at 10 K exhibited a series of exciton emission peaks at 3.359-3.376 eV with full width at half maximum (FWHM) values of 1-3 meV. The origins of the emission peaks were confirmed by a series of PL measurements with varying temperatures. The observation of the free exciton peak for ZnO nanorods at 10 K strongly suggests that the nanorods are of high purity as well as low defect concentration. In addition, time-resolved PL property of free exciton peak will also be discussed. The ability to grow high purity ZnO nanorods is expected to greatly increase the versatility and power of these building blocks for applications in nanoscale photonics and electronics.

P9.54

PARALLEL BIAS-ENHANCED CHEMICAL VAPOR DEPOSITION OF SULFUR-DOPED MICROCRYSTALLINE DIAMOND AND NANOCRYSTALLINE CARBON THIN FILMS. Joel De Jesús, Department of Physics, University of Puerto Rico, San Juan, PR; Juan A. González, Department of Physics and Electronics, University of Puerto Rico, Humacao, PR; Oscar O. Ortiz, Department of Chemical Engineering, Polytechnic University, San Juan, PR; Brad R. Weiner, Department of Chemistry, University of Puerto Rico, San Juan, PR; Gerardo Morell, Department of Physical Sciences, University of Puerto Rico, San Juan, PR.

The compositional and microstructural transformations induced by parallel bias-enhanced chemical vapor deposition of sulfur-doped microcrystalline (μ c-D:S) and nanocrystalline carbon (nC:S) were investigated by Raman spectroscopy (RS), scanning electron microscopy (SEM), atomic force microscopy, and X-ray photoelectron spectroscopy (XPS). The films were deposited in a hot filament chemical vapor deposition (HFCVD) system using CH₄, H₂ and H₂S. Sulfur-doped microcrystalline and nanocrystalline films with different microstructure were prepared by changing the substrate temperature (300-900°C), the CH₄ concentration (0.3 and 2.0%) and the H₂S concentration (0 and 500 ppm). Two parallel plates on the sides of the substrate holder were used in order to apply a bias voltage in the range of 0-1000 VDC parallel to the substrate surface. The parallel bias has the effect of removing a significant portion of the charged particles and species present during the chemical vapor deposition, while avoiding particle bombardment of the film surface. Moreover, charge accumulation near the growing film can be minimized by this method. The study revealed a significant improvement in the films' density, and changes in their morphology and carbon bonding composition as a function of parallel bias. These changes are discussed in terms of the mechanism of carbon film deposition in the chemical vapor environment.

P9.55

DIFFUSION MECHANISM FOR SELF ASSEMBLY ON INHOMOGENEOUSLY STRAINED SURFACES. M.I. Larsson^{a,b}, R.F. Sabiryanov^c, K. Cho^d, and B.M. Clemens^a; ^aDepartment of Materials Science and Engineering, Stanford University, Stanford, CA; ^bon leave from Department of Physics, Karlstad University, SWEDEN; ^cDepartment of Physics, University of Nebraska at Omaha, Omaha, NE; ^dDepartment of Mechanical Engineering, Stanford University, Stanford, CA.

Growth of nanostructures with controlled shape on inhomogeneously strained surfaces is addressed. The fundamental issues of self assembly are investigated by means of kinetic Monte Carlo (KMC) simulations. We show that the driving force for self organization can be explained in terms of kinetically and thermodynamically driven surface diffusion. The local strain dependence of the valley- and bridge-site energies determines the dominant type of surface diffusion. Various energy-strain dependencies and the resulting surface diffusion properties are addressed and exemplified with KMC simulations. The KMC model is a full diffusion bond-counting model including nearest neighbor as well as second-nearest neighbor interactions with an event catalogue consisting of 9393 events modeling the effects of strain

modified surface energies. The surface-strain energies in this study are caused by either periodic strain fields or parabolic strain as a function of distance across a Pt nanowire of width ~ 10 -20 nm. How the surface diffusion and the self organization of deposited Ag are influenced by altering the adatom energy-strain dependence will be discussed. The valley and bridge site energies for Ag on Pt(111) were calculated using density functional theory. This work does not only report on the mechanism of self assembly but also suggests a method to control the width of nanowires.

P9.56

MONTE CARLO SIMULATION OF PHASE SEPARATION IN NONSTOICHIOMETRIC SILICA. V.M. Burlakov, G.A.D. Briggs, A.P. Sutton, Department of Materials, University of Oxford, Oxford, UNITED KINGDOM; A. Bongiorno and A. Pasquarello, Institut de Théorie des Phénomènes Physiques (ITP), EPFL, Lausanne, SWITZERLAND and IRRMA, Lausanne, SWITZERLAND.

Using our recent model for a network material with coordination defects [1] we have simulated the annealing of bulk nonstoichiometric silica and an amorphous SiO₂/SiO/SiO₂ superlattice. Sub-oxide penalty energies [2] as well as a dependence of the silicon dangling bond energy upon the oxidation state of the silicon atom were taken into account. Upon annealing of SiO_x a tendency to phase separation into pure a-Si and SiO₂ has been observed. Comparison between annealed bulk SiO and a SiO₂/SiO/SiO₂ superlattice revealed sharp localization of 0- and 1-fold oxidized Si atoms toward the middle of the SiO layer of the superlattice, while those in the bulk SiO are distributed over the whole sample volume forming a network. The observed sharp localization of the Si phase within the SiO layer is interpreted as the initial stage of crystallization, which has been experimentally observed in amorphous SiO₂/SiO/SiO₂ superlattices [3]. A description of the phase separation process is discussed.

1. V.M. Burlakov, G.A.D. Briggs, A. P. Sutton, Y. Tsukahara, Phys. Rev. Lett. **86**, 3052 (2001).
2. A. Bongiorno, A. Pasquarello, Phys. Rev. B **62**, R16 326 (2000).
3. M. Zacharias, J. Heitmann, U. Goesele, MRS Bulletin, p. 975, Dec. 2001.

P9.57

FORMATION OF LUMINESCENT Si NANOCRYSTALS BY HIGH-TEMPERATURE ANNEALING OF ION-BEAM-SPUTTERED Si/SiO₂ MULTILAYERS. Suk-Ho Choi and Jun Sung Bae, Kyung Hee Univ, College of Electronics and Information and Inst of Natural Sciences, Suwon, KOREA; Kyung Jung Kim, Dae Won Moon, Korea Research Inst of Standards and Science, Nano Surface Gr, Taejeon, KOREA.

Si/SiO₂ multilayers (MLs) have been prepared under various conditions of Si layer thickness and deposition temperature by ion beam sputtering. The annealing at temperatures $\geq 1100^\circ\text{C}$ leads to the formation of Si nanocrystals in the Si layer of MLs. The high resolution transmission electron microscopy images clearly demonstrate the existence of Si nanocrystals, which exhibit photoluminescence (PL) in the visible range when a-Si/SiO₂ MLs are deposited at temperatures $\geq 300^\circ\text{C}$. This is attributed to the decrease of the non-radiative recombination centers in the interface between Si nanocrystal and surface oxide. The increase of deposition temperature enhances the PL intensity and shifts its peak to higher energy. The visible PL is believed to result from the quantum confinement effect of Si nanocrystals, which are discussed with reference to the data of structural analysis.

P9.58

APPLICATION OF BISMUTH NANOLINES AS ATOMIC WIRES IN MOLECULAR ELECTRONICS: THEORETICAL ANALYSIS. Rodion V. Belosludov^a, Amir A. Farajian^a, Hiroshi Mizuseki^a, Yoshiyuki Kawazoe^a, K. Miki^b. ^aInstitute for Materials Research, Tohoku University, Sendai, JAPAN; ^bNanotechnology Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 4, Tsukuba, Ibaraki, JAPAN.

For application to molecular electronics, the atomic wires on semiconductor surfaces can be an important component because it can be used as power supply line or ground line connecting a metal electrode and single molecular devices to create complex molecular circuits. Development of scanning tunneling microscopy and recent remarkable progress in its application for atom manipulation and surface modification allow one to fabricate various atomic-scale artificial structures. Bismuth nanowires on Si(001) surface has been realized and these nanolines have a several hundreds of nanometers length without kink or defect [1,2]. In order to integrate Bi nanolines into complex molecular circuits, it is important to measure conductance characteristics of such wires. One of the problems, which can arise before these measurements, is the understanding the surface effect on value of current through these wires and hence to prevent

the possible current leakage. In order to answer on this question the electronic properties of the bismuth nanolines structure have been examined using density functional theory at the B3PW91/LanL2MB level of theory. Moreover, the detailed analysis of electron distribution for unoccupied orbitals has been done since the incoming electrons are assumed to pass through these orbitals. The obtained results demonstrate that the formation of dangling bonds on Si surface has negative effect on current through the deposited metallic atomic wires, resulting in possible current leakage across these dangling bonds. It can be suggested to use the hydrogen terminated Si(001) surface in order to realize the Bi lines as an active atom-wire interconnections for molecular electronics applications. [1] K. Miki, J.H.G. Owen, D.R. Bowler, G.A.D. Briggs and K. Sakamoto: Surf. Sci. 421 (1999) 397. [2] J.H.G. Owen, K. Miki, H. Koh, H.W. Yeom and D.R. Bowler: Phys. Rev. Lett. **88** (2002) 226104.

P9.59

SYNCHROTRON X-RAY SCATTERING TECHNIQUE ON THE STUDY OF SEMICONDUCTOR QUANTUM DOTS. Yu. P. Stetsko, K.S. Liang, C.H. Hsu, M.T. Tang, Research Division, Synchrotron Radiation Research Center, Hsinchu, TAIWAN; D.Y. Noh, Department of Material Science and Engineering, Kwangju Institute of Science and Technology, KOREA.

Using synchrotron x-ray technique, the studies of the structure of semiconductor quantum dots have been reported. In this work, the x-ray method is further developed. It based on the study of diffracted intensity from quantum dots at the absorption edges of involved atoms. This technique essentially enhances the accuracy of determining the composition and lattice parameter distributions along a height of quantum dots. A theoretical model for analysis of the spatial and the spectral distributions of diffracted intensity is proposed. The theoretical results are compared with experimental ones. This technique is successfully approved for self-assembled InGaAs/GaAs quantum dots grown by molecular-beam epitaxy.

P9.60

HIGH-POWER AND BROAD-BAND QUANTUM-DOT SUPERLUMINESCENT DIODES. Z.Y. Zhang, Z.G. Wang, B. Xu, Z.Z. Sun, P.Jin, X.Q. Meng, Ch.M. Li, Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, P.R. CHINA.

Superluminescent diodes (SLD) are the optimum light sources for application in optical measurement systems such as fiber gyroscope and optical time domain reflectometers (OTDR). So far, however, few groups have attempted to broaden the emission spectral width of SLD. As the spectral width is broadened, the coherence length is reduced. A short coherence length can reduce the Rayleigh backscattering in fiber gyroscope systems and can improve the spatial resolution in OTDR application. In recent years, quasizero dimensional system, especially self-assembled semiconductor quantum dots (QDs) grown by Stranski-Krastanow mode has been investigated from a fundamental physics point of view and for the potential device applications such as laser diodes. But in current self-assembled quantum dots technology, certain size inhomogeneity is common and typically uniformity better than 90% is difficult to achieve. In general, such inhomogeneous size distribution of SAQD in the active region is disadvantageous for achieving lasing of QD laser. The coherence length L_{coh} of SLD is given by $L_{coh} = \lambda^2 / \Delta\lambda$ where $\Delta\lambda$ is the emission spectral width of the SLD and λ is its central wavelength, so for the designed self-assembled quantum-dot superluminescent diodes (SAQD-SLD), it becomes an effective, intrinsic advantage for broadening spectrum. Moreover, since the changing of energy of SAQD is continuous, the flat spectrum can be realized and it will be good for WDM and other applications of SLD. In this report, the tilted-stripe SLDs were fabricated on the MBE grown wafer with multiple layer stacked QD structure. Because the tilted-stripe structure could well eliminate the Fabry-Perot resonance, and the multiple stack QD active region could not only do benefit to broaden the spectral width, but also enhance the quantum efficiency, the high-power and broad-band SLD has been easily realized. At last, the CW output power of above 200mW with the spectral bandwidth of above 60nm was obtained of the SAQD-SLD at room temperature.

P9.61

FORMATION OF SELF-ASSEMBLED MONOLAYERS OF 12-(3-THIENYL)DODECANETHIOL ON GOLD AND THEIR INTERACTION WITH VAPOR-DEPOSITED ALUMINUM. Heejeon Ahn and James E. Whitten, The Department of Chemistry and Center for Advanced Materials, The University of Massachusetts Lowell, Lowell, MA.

Self-assembled monolayers (SAMs) of a thienyl-terminated alkanethiol, 12-(3-thienyl)dodecanethiol, have been formed on gold surfaces. X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) demonstrate the formation of monolayers attached to the gold

surface via thiolate bonds, with thiophene rings at the periphery of the assemblies. The thickness of the monolayer is 17.3 Å, as estimated by ellipsometry. Dynamic contact angle measurements show advancing and receding water contact angles of 90° and 76°, respectively. Quartz crystal microbalance measurements indicate that the monolayer has a packing density of 5.2×10^{14} molecules/cm². The interaction of thermally deposited aluminum with the SAM has also been investigated. C 1s and Al 2s XPS spectra indicate electron transfer from aluminum to the thiophene rings. For comparison, aluminum has also been deposited on SAMs of 1-tridecanethiol. C 1s spectra do not indicate reaction of aluminum with the alkyl chains, but Al 2s spectra are consistent with penetration of Al atoms into the Au-S bond. In the case of 12-(3-thienyl)dodecanethiol, He I UPS valence electronic spectra demonstrate strong interaction with aluminum and that metal penetration is much less dramatic than in the case of the alkanethiol.

P9.62

SELF-ASSEMBLY OF NANOPARTICLES BY A NOVEL FREEZE-DRYING METHOD. Dongling Ma, Linda S. Schadler, Richard W. Siegel, Dept of Materials Science and Engineering, Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY.

Capped microtubes consisting of titanium dioxide (TiO₂) nanoparticle building blocks were synthesized for the first time by a novel freeze-drying method following nanoparticle size refinement. Field emission scanning electron microscopy (FESEM) showed that most tubes are about one micron in diameter and have a high aspect ratio. Both inside and outside surfaces appear quite smooth, although at high magnification, the constituent nanoparticles are seen clearly. More interesting is that most tubes possess a low-energy, end-cap structure. The chemical nature of the TiO₂ tubes was confirmed by energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. It was found that the Ti/O ratio is different from tube to tube, while the average Ti/O ratio is the same for both as-received nanoparticles and tubular TiO₂. X-ray diffraction spectroscopy was used to investigate the crystal structure. Both concentration and pH of the solution have an important influence on the resulting self-assembled structures. The process of self-assembly of the nanoparticles is most likely driven by capillarity and aided by hydrogen bonding between the nanoparticles and solvent molecules during freeze-drying.

P9.63

SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE CAPPED NANOPARTICLES. Maria Francesca Casula, Young-wook Jun and Paul Alivisatos, Department of Chemistry, University of California, Berkeley, CA.

The synthesis of iron oxide nanoparticles is of interest as a result of their potential use as media for magnetic data storage, in catalysis and in the preparation of ferrofluids. In particular, one of the key issues is to obtain uniform nanoparticles since many properties are size-dependent. A further intrinsic problem in the controlled synthesis of iron oxides is related to the occurrence of different oxidation states and polymorphs. From this standpoint, a non-hydrolytic approach shows the advantage of avoiding the complex aqueous chemistry of iron, which is strongly pH and counter-ion dependent. In particular, it is likely that by avoiding the formation of hydroxy- and oxyhydroxy species, which can in turn possibly transform in at least two oxides, a high degree of control over the synthesis could be achieved. In this work, the synthesis of iron oxide nanoparticles was performed using pentacarbonyl iron and 3-chloroperoxybenzoic acid as precursors. The precursors were rapidly injected in a hot surfactant under inert atmosphere and the inorganic particles were precipitated from ethanol. The capped nanoparticles are soluble in nonpolar solvents such as toluene. The crystal structure was studied by X-Ray powder diffraction, selected area electron diffraction and microdiffraction. No further heat treatment was needed to achieve high crystallinity. Conventional and high resolution transmission electron microscopy and atomic force microscopy were used to investigate the shape, the size and the size distribution of the nanoparticles. The nanocrystals exhibit extremely narrow size distribution and have a disk shape. The effect of the iron precursor, the surfactant and the oxidizer relative molar ratios on the nanoparticle formation was investigated in order to determine the conditions allowing to obtain monodisperse iron oxide single crystals. References: 1 R.F. Ziolo, E.P. Giannelis, B.A. Weinstein, N.M. O'Horo, B.N. Ganguly, V. Mehrotra, M.W. Russell and D.R. Huffman, *Science* 1992, 257, 219; M.D. Bentzon, J. van Wontergem, S. Morup, A. Tholen and C.J.W. Koch, *Phil. Mag. B*, 1989, 60, 169. 2 R. Zboril, M. Mashlan and D. Petridis, *Chem. Mater.* 2002, 14, 969. 3 R.M. Schwertmann and U. Cornill, *The Iron Oxides*, Weinheim, New York, 1996.

P9.64

CONTROLLING 2-DIMENSIONAL GROWTH OF SILVER NANOPLATES. Sihai Chen and David L. Carroll, Clemson Univ, School of Materials Science & Engineering, Clemson, SC.

A new solution-phase approach has been developed for the control of silver nanoplate dimension. In this method, using cetyltrimethylammonium bromide (CTAB) as the soft templates, silver nanoplates with a thickness of the order of 30 nm, side edge as large as 300 nm have been obtained. Several methods including transmission electron microscopy, scanning electron microscopy and atomic force microscopy have been used to characterize their dimensions. X-ray and electron diffraction analysis reveal that these nanoplates are single crystal and with its basal plane as (111) lattice plane. We show that the surface plasmon absorption band of silver nanoplates can be extended into whole visible ranges. The formation of self-assembled monolayer of CTAB on the basal plane is suggested to account for both the anisotropic growth and the formation of large-scale stacking nanostructures.

SESSION P10: SYNTHESIS, ASSEMBLY, AND APPLICATION OF NANO-BUILDING BLOCKS I
Friday Morning, April 25, 2003
Metropolitan III (Argent)

8:30 AM P10.1

DIAMETER-CONTROLLED GROWTH OF SINGLE-CRYSTALLINE In₂O₃ NANOWIRES AND THEIR ELECTRONIC PROPERTIES. Chao Li, Daihua Zhang, Song Han, Xiaolei Liu, Tao Tang, and Chongwu Zhou, Univ. of Southern California, Dept of Electrical Engineering and Electrophysics, Los Angeles, CA.

One-dimensional nanostructured systems have recently attracted much attention due to their novel properties and great potential applications in numerous areas such as nanoscale electronics and photonics. Among them, In₂O₃ as a wide bandgap transparent semiconductor and potential ultra-sensitive toxic gas detectors is becoming increasingly important. We have developed a novel approach to synthesize single crystalline In₂O₃ nanowires using a laser ablation method. Extensive material characterization such as X-ray diffraction (XRD) and selected area electron diffraction (SAED) indicate the single crystalline cubic structure of these nanowires with [110] as the growth direction. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used to decide the nanowires diameter and length. By using monodispersed gold clusters as the catalyst, these nanowires can be grown with well-defined diameters around 10 nm, 20 nm and 30 nm, respectively. Individual In₂O₃ nanowires have been utilized to construct field effect transistors, which confirmed In₂O₃ nanowires as n-type semiconductors and exhibited on/off ratios up to 1000. Our work can lead to important applications such as chemical sensing for In₂O₃ nanowires.

8:45 AM P10.2

PATTERNING HETEROGENEOUS ARRAYS OF SUPERPARAMAGNETIC PARTICLES. B. Yellen and G. Friedman, Drexel University, Electrical and Computer Engineering Department, Philadelphia, PA.

Planar arrays of colloidal particles have been utilized in devices and materials for photonic, electronic, magnetic and sensor applications. Several different methods for patterning colloidal particles arrays have emerged in recent past, including surface chemistry, electrostatic, and surface tension driven assembly of colloidal particles. In contrast with these methods, magnetic template driven assembly offers significant advantages. The main advantage is that the highly non-linear behavior of magnetic materials can be exploited to generate both attractive and repulsive forces on colloidal particles. The ability to generate repulsive forces, in particular, opens the possibility for assembling particle arrays with controlled defects. Theoretical and experimental studies of magnetic template driven assembly of superparamagnetic colloidal particles will be presented. Experimental arrangements have used an array of ferromagnetic islands, fabricated through conventional photolithographic lift-off process, to attract magnetic beads from colloidal suspension. Several experimental arrangements have been investigated. One arrangement features an array of magnetized Cobalt islands decorated with 2.8 μm or 7.1 μm beads. The results support theoretical predictions that small beads are attracted to the poles of the island whereas large beads tend towards the center of the island. Another arrangement features a protective layer of micro-wells aligned over the ends of the ferromagnetic islands used to better control the spatial distribution of beads that populate template. This arrangement can exploit external uniform magnetic field bias applied perpendicularly to the substrate to promote micro-wells to be either vacant or populated by a single bead, depending on the orientation of the external magnetic field with respect to the field produced by the exposed ferromagnetic pole. Experiments will be shown to confirm theoretical predictions of such behavior.

9:00 AM *P10.3**NOVEL STRUCTURE OF FULLERENES AND ENDOHEDRAL METALLOFULLERENES.** Chun-Ru Wang and Chun-Li Bai,

Institute of Chemistry, Chinese Academy of Sciences, CHINA; Hisanori Shinohara, Department of Chemistry, Nagoya University, JAPAN; Lothar Dunsch, Institute fuer Festkoerper- und Werkstofforschung, Dresden, GERMANY.

By using Kraetschmer-Huffman synthesis and HPLC separation methods we have isolated a series of novel fullerenes and endohedral fullerenes. Various spectroscopic techniques, e.g., MS, XPS, NMR, UV-vis-NIR, IR, Raman, X-ray diffraction spectrometry etc., were adopted to characterize the isolated fullerenes. Several fullerenes were revealed to hold novel structures and electronic properties. For examples, C₈₀(D_{5d}) was isolated and characterized to have an ellipsoidal structure which is in fact one of the shortest SW-nanotubes; The isolation of Sc₂@C₆₆ breaks the well-known isolated-pentagon-rule (IPR) for the first time, it shows that the untraditional fullerenes may be dramatically stabilized through encaging one or several metal atoms; Sc₂C₂@C₈₄ is a novel molecular endohedral fullerene in which the Sc₂C₂ cluster rotates rapidly along the main C₂ axis of C₈₄(D_{2d}). This fullerene is predicted to be a molecular magnet and may be used as nano-switch in electronics. Recently we successfully synthesized a carbene endohedral fullerene CH₂@C₇₀ for the first time. The smallest carbene molecule CH₂ was stably encaged by the C₇₀ fullerene, and maintains both its geometrical and electronic structures of free CH₂ inside fullerene cage.

9:30 AM P10.4

SELF-ASSEMBLY OF SEMICONDUCTING OXIDE NANOWIRES, NANORODS AND NANORIBBONS. J.G. Wen^{a,b}, J.Y. Lao^b, Y.L. Foo^a, Z.F. Ren^b, I. Petrov^a. ^aFrederick Seitz Materials Research Lab, Univ. of Illinois at Urbana-Champaign, Urbana, IL; ^bDept of Physics, Boston College, Chestnut Hill, MA.

We have synthesized self-assembled ZnO-based nanoscale heterostructures such as nanoribbons (with a core), nanocombs, and nanorods. This has been realized through the addition of alloying elements (In or Sn) during the vapor phase transport and condensation deposition process. Each nanoscale heterostructure consists of a faceted nanowire core, with side branches (nanoribbons or nanorods) emanating from facets of the central nanowire core. For example, nanorods consist of In₂O₃ central nanowire core and ZnO side nanorods. We found that the symmetry of nanorods depends on the crystallographic orientation of In₂O₃ central nanowire core. When the In₂O₃ nanowires grow along [001] and [111] direction, the resulting nanorods have 4- and 6-fold symmetry, respectively. The central nanowire core can be either ZnO, (ZnO)₁₁In₂O₃, or In₂O₃, depending on incoming flux composition ratio. The physical mechanism of branching stems from segregation of alloying elements to facets during the growth of the nanowire core, thus creating nucleation sites for side branches. This self-assembly mechanism can also be applied to other similar semiconducting oxide systems, thus opening a novel approach for synthesizing sophisticated nanoscale heterostructures for nanodevices.

9:45 AM P10.5

SELF-ASSEMBLY OF PbSe NANOPARTICLES INTO NANORINGS. Weijie L. Zhou, Jibao He, Jiye Fang, Tuyet-Anh Huynh, Trevor J. Kennedy, Kevin L. Stokes, and Charles J. O'Connor.

In this presentation, we report a self-assembly of monolayer and multilayer nanorings of PbSe nanoparticles. PbSe nanoparticles were synthesized by using a combination approach of reduction and thermal decomposition. The nanoparticles are about 5 nm and appeared as truncated octahedral enclosed by the {100} and {111} crystal facets of fcc structure. The large area monodisperse self-assembly nanoarrays were obtained by dropping the high concentration solution of PbSe nanoparticles on the carbon grid. The nanoparticles has hexagonal close packing and orient randomly in the nanoarrays. By diluting the solution for large area self-assembly, self-assembly of monolayer and multilayer nanorings can be achieved. The nanoring formation is determined by hydrodynamics, surface effects, and interaction between the nanoparticles and carbon grid.

10:30 AM *P10.6

STRUCTURES OF FE-PT MAGNETIC NANOCRYSTAL SELF-ASSEMBLED ARRAYS AND THE OPTIMIZATION OF MAGNETIC PROPERTIES. Jing Li and Zhong L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA; Hao Zeng and Shouheng Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY; J.-P. Liu, Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA.

Depending on the Fe to Pt elemental ratio, the Fe-Pt alloys can display chemically disordered face centered cubic phase or chemically ordered phases. We report detailed microscopic studies on structures

of Fe-Pt nanocrystal based self-assembled nanocomposite. We have characterized the nanometer-scale interfaces between the magnetically hard and soft phase for the Fe-Pt based nanocomposites formed by self-assembly of nanoparticles of different sizes. Annealing the composite under reducing atmosphere at 600°C and 700°C induced, in addition to the hard L10 (fcc) FePt phase, magnetically soft Fe-rich phase of Fe₃Pt. The FePt and Fe₃Pt phases were either linked by a common grain boundary or co-existed within a common grain as domains with sizes < 10 nm. The coalesced larger particles have different structures for different annealing temperatures, corresponding to different magnetization mechanisms. Controlled annealing results in metallic composites with magnetically hard and soft phase exchange coupled. The approach offers precise engineering control on the dimension of the components and their nanoscale interactions in the composite, rendering isotropic FePt-based nanocomposites with superior magnetic properties [1].

[1] Hao Zeng, Jing Li, Zhong L. Wang, J.-P. Liu & Shouheng Sun, Nature, in press (2002).

11:00 AM P10.7

USING PHASE SEGREGATION OF ORGANIC MOLECULES AND INORGANIC NANOCRYSTALS IN LAYERED OPTOELECTRONIC DEVICE FABRICATION. Jonathan Steckel, Mounji Bawendi, Massachusetts Institute of Technology, Department of Chemistry, Cambridge, MA; Seth Coe, Vladimir Bulović, Massachusetts Institute of Technology, Department of Electrical Engineering and Computer Science, Cambridge, MA.

Precise control of the placement of active elements in nanostructured devices is crucial for controlling and optimizing device parameters and for understanding their fundamental physical properties. We describe a method of generating large area (cm²), well defined layered structures of semiconductor nanocrystal quantum dots (QDs) and semiconducting organic molecules for the creation of hybrid organic/inorganic electronic and optoelectronic devices. Bilayers consisting of an ordered single monolayer of QDs on a submicron layer of an organic semiconductor are created using a single spin-casting step. The QDs form hexagonally close packed, ordered domains on the scale of microns. We find that nanostructured QD light emitting devices using this technique exhibit far higher efficiency and brightness than disordered hybrid QD-LEDs. The QD monolayer is created when the QDs capped with aliphatic groups phase segregate from the aromatic organic materials during the spin-casting process. We observe this process using several different organic molecules, as well as with different QD core and cap materials. The reproducibility and precision of this technique suggests it as a general fabrication method, with wide applicability to the fabrication of other nanostructured devices such as photodetectors, memory cells, and single electron transistors.

11:15 AM P10.8

SELF-ASSEMBLED COBALT NANOPARTICLE DISPERSIONS IN THE PRESENCE OF POLYSILOXANE BLOCK COPOLYMERS. Sheng Lin-Gibson, Vivek M. Prabhu, Charles C. Han, Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD; Metha Rutnakornpituk, Judy S. Riffle, Dept of Chemistry, Virginia Tech, Blacksburg, VA.

Stable suspensions of superparamagnetic cobalt nanoparticles have been prepared in poly(dimethylsiloxane) (PDMS) carrier fluids in the presence of poly[dimethylsiloxane-block-(3-cyanopropyl)methylsiloxane-block-dimethylsiloxane] triblock copolymers as steric stabilizers. These novel triblock copolymers with polar nitrile-functionalized central blocks form stable micelles above the critical micelle concentration in toluene. Micelle solutions are subsequently used as nanoreactors for the thermal decomposition of Co₂(CO)₈ precursor. We have examined factors that determine the particle size and reaction yield, such as micelle concentration, cobalt to micelle ratio, and solution structures formed by triblock copolymers with different central block length. The particle size is sensitive to the copolymer to cobalt ratio while the micelle solution structures affect the easy of cobalt nanoparticle formation. The micellar solution morphology was determined by small-angle X-ray scattering (SAXS) and neutron scattering (SANS). The 15k-5k-15k copolymer forms spherical micelles as determined by both model fitting of the SANS scattering data with a core-corona structure factor and a q⁻⁴ scattering power law, where q is the scattering wave vector. Micelles formed by the 15k-2k-15k copolymer showed complicated scattering forms superimposed by the structures of micelles and solvated chains, but also produced larger cobalt particle yield. The micelle size varies weakly with concentration (between 1 gL⁻¹ and 50 gL⁻¹) and temperature over the range of 25°C to 100°C. The latter indicates the thermal stability of the micelles for subsequent inorganic nanoparticle formation conditions. These results are important for deciding what solution structures form better cobalt coatings.

11:30 AM *P10.9

HIGHER DIAMONDoids: DIAMOND MOLECULES WITH POTENTIAL IN NANOMATERIALS APPLICATIONS. Jeremy E. Dahl, Shenggao Liu, and Robert M. Carlson, MolecularDiamond Technologies, ChevronTexaco Technology Ventures.

Hydrogen-terminated diamonds form a continuous series beginning with macroscopic diamonds, microscopic diamonds including CVD diamonds, nanometer-sized diamonds down to ~ 3 nm, and finally to diamondoid hydrocarbons less than 1 nm including adamantane, diamantane and triamantane. All these forms have been previously available with the exception of higher diamondoids, hydrogen-terminated diamonds in the ~ 1 to ~ 2 nm range, which we now provide. It is in this size range that interesting transitions in properties are likely to be found. We have identified and isolated higher diamondoids (C22 and higher polymantanes) including tetramantanes, pentamantanes, hexamantanes, heptamantanes, octamantanes, nonamantanes, a decamantane and an undecamantane from petroleum. These molecules contain from four to eleven diamond crystal cages. Exceptional thermal stability and diverse geometries make possible their isolation from petroleum. Structures were proven by single crystal X-ray crystallography for selected members of three families of higher diamondoids. As members of the H-terminated diamond series, these molecules have great strength and rigidity, but they also show a remarkable variety of 3-dimensional shapes, including resolvable chiral forms (some with unusual primary helical structures, where the helicity is built into the backbone of the molecule, rather than arising from steric effects, such as in the helicenes). Properties of higher diamondoids can be tuned by the attachment of various functional groups, allowing customized mechanical, electronic and biomedical properties.

SESSION P11: SYNTHESIS, ASSEMBLY, AND APPLICATION OF NANO-BUILDING BLOCKS II
Friday Afternoon, April 25, 2003
Metropolitan III (Argent)

1:30 PM *P11.1

REPLICATION OF NANOSTRUCTURED CARBONS WITH SELF-ASSEMBLED SILICA TEMPLATES. Sang Hoon Joo, Tae-Wan Kim, In-Soo Park, Minkee Choi and Ryong Ryoo, Department of Chemistry, Korea Advanced Institute of Science and Technology Daejeon, KOREA.

Molding is a common technique that was used for a long time for fabrication of objects with desired shapes and sizes on the macroscopic scale. In recent years, there were remarkable advances in the molding strategy toward the fabrication of nanostructured materials. Here we show that various types of nanostructured carbon can be obtained using silica templates, which are synthesized via the organic-inorganic self-assembly processes. These materials include not only the macrostructured carbons but also mesostructured carbons, and even microporous carbons can be fabricated using zeolites. It is particularly noteworthy that the structure of the carbon frameworks can be controlled widely, ranging from amorphous to graphitic. For example, we can synthesize ordered mesoporous carbons characteristic of the graphitic framework structure. We present such advances for the fabrication of nanostructured carbon materials. We believe that the nanostructured carbons thus fabricated would attract much attention in modern science and technologies including purification, separation, catalysis, electrochemistry and energy storage.

2:00 PM P11.2

Abstract Withdrawn.

2:15 PM P11.3

FOCUSED ION BEAM MICROPATTERNING AS A BUILDING BLOCK TO CONTROL SELF ASSEMBLED QUANTUM DOT FORMATION. M. Kammler[†], F.M. Ross, and R. Hull[†], [†]University of Virginia, Department of MSE, Charlottesville, VA; IBM T.J. Watson Research Center, Yorktown Heights, NY.

Self-assembly of quantum dots has emerged as a successful method for forming nanoscale structures showing new functionality with promising application in device technology. We demonstrate that the position of quantum dots can be controlled on a nanoscale by in situ patterning with a focused ion beam (FIB) overcoming the random nature of the self-assembly process opening new possibilities in device applications such as quantum cellular automata. Irradiation, annealing and Ge growth processes on a Si(001) surface were studied in an ultra high vacuum system combining a FIB column with an ultra high vacuum transmission electron microscope (UHV-TEM) allowing us to pattern Si surfaces on a nm-scale using a Ga⁺ ion beam. After patterning the sample using the FIB it is transferred under UHV into the UHV-TEM to study the annealing process of the

FIB-sputtered regions and their effect on the nucleation, growth and structure of Ge islands, in real time, during chemical vapor deposition of digermane carried out in the microscope polepiece. We observed, that epitaxial Ge islands grow selectively at Ga-irradiated regions, allowing patterned arrays of islands to be created. At low doses of 6000 Ga ions per spot (<100nm in diameter), chemical effects of the implanted Ga or strain due to buried defects are responsible for the selective growth since annealing restores the initial flat surface. At higher doses, topographic effects produced by sputtering and redeposition control the selective nucleation. Islands grown on irradiated areas are significant smaller and steeper than islands grown on clean Si(001), suggesting a strong surfactant effect of Ga. In conclusion, we show that nanoscaled prepatterning of the Si substrate with the FIB allows direct control of individual Ge quantum dot nucleation sites, with precision of tens of nanometers, and at writing rates that scale to 10⁴ features per second.

2:30 PM P11.4

ELECTROSTATIC SELF-ASSEMBLY OF METAL AND SEMICONDUCTOR NANOPARTICLES IN POLYELECTROLYTES: FACTORS GOVERNING THE ASSEMBLY, AND PHOTOELECTROCHEMICAL BEHAVIOR. Sarah Ghannoum, Marie-Zabel Markarian, Jad Jaber, and Lara I. Halaoui, Department of Chemistry, American University of Beirut, Beirut, LEBANON; Yan Xin, National High-Magnetic Field Laboratory, Florida State University, Tallahassee, FL.

The electrostatic self-assembly of hetero-nanostructured multilayers of metal and semiconductor nanoparticles in polyelectrolytes, the kinetics of self-assembly, and the photoelectrochemical properties of the assembled films were investigated. Polyacrylate-capped Pt (2.5 \pm 0.6 nm) and Q-CdS nanoparticles (3.6 \pm 0.5 nm) were synthesized and self-assembled layer-by-layer in poly(diallyldimethylammonium chloride) by virtue of the Coulombic attraction between the negatively charged capping agent and the cationic polyelectrolyte. The density of nanoparticles self-assembled per layer and the kinetics of adsorption on PDPA were found to depend on the ionic strength and the composition of the nanoparticles solution, and on the number of rinsing/drying cycles (for the same total dipping time). Photoelectrochemical and electrical measurements of Q-CdS/PDPA films revealed the feasibility of charge transport and photocurrent generation in the films, likely by means of charge hopping between the Q-particles through the embedding matrix. Anodic or cathodic photocurrents were generated at the nanostructured films depending on the applied electrode potential; this is attributed to the quantized properties of the quantum dots. Photocurrent magnitudes increased with increasing particles loading only up to 4-bilayers, believed to be caused by photogenerated carrier losses as films get thicker. The potential at which the photocurrent reversed in direction from anodic to cathodic is reported to shift by -66 mV per pH unit, similar to the shift in V_{fb} of bulk CdS. This was found to be partly due to an increase in the reducing power of the QD electron with increasing pH, as indicated from photocurrent-voltage plots acquired in the presence of methyl viologen.

2:45 PM P11.5

HIGH-YIELD SOLVOTHERMAL FORMATION OF MAGNETIC ALLOY NANOWIRES. Zongtao Zhang, Douglas A. Blom, Zheng Gai, James R. Thompson, Jian Shen, Sheng Dai, Chemical Sciences and Solid State Divisions, Oak Ridge National Laboratory, Oak Ridge, TN.

One-dimensional (1D) nanostructured materials have attracted much attention concerning their potential applications in both the investigation of mesoscopic physics and the fabrication of nanodevices. In particular, 1D magnetic nanomaterials have been extensively exploited for their potential utilization in magnetic recording and spintronics. The key synthetic methodologies developed so far include catalyzed high-temperature growth via the vapor-liquid-solid (VLS) mechanism, templated synthesis, and direct electrochemical precipitation. Nevertheless, it remains a challenge to prepare free-standing magnetic nanowires in high yield. Solvothermal synthesis is one of the most powerful strategies employed for the crystallization of many unique compounds. Under solvothermal conditions, many starting materials can undergo quite unexpected reactions, which are often accompanied by the formation of nanoscopic morphologies that are not accessible by classical routes. Here, we report the first successful synthesis of an interesting 1D ferromagnetic alloy by direct through a solvothermal reaction. The alloy nanowires obtained have a tunable diameter of 10 to 50 nm and a length along the longitudinal axis of up to several microns, depending on crystallization temperature and time. A unique formation mechanism involving coarsening and ripening under solvothermal conditions was discovered. An unusually high magnetic moment was found for this new 1D material relative to that of the bulk material.

3:30 PM P11.6
SUPERCRITICAL FLUIDS AS NEW REACTION MEDIA TO SYNTHESIZE NANOSTRUCTURED MATERIALS. Cyril Aymonier, Sophie Desmoulins-Krawiec, Anne Serani, Francois Weill, Francois Cansell, Bordeaux Univ, Institut of Condensed Matter Chemistry (ICMCB), Pessac, FRANCE.

Supercritical fluids exhibit a range of unusual properties that can be exploited for the development of new reactions which are different from those performed in classical solid state chemistry. The main interest of supercritical fluids as reaction media to synthesize nanostructured materials is the possibility to tune continuously the fluid properties from gas to liquid with small pressure and temperature variations. Moreover, supercritical fluid processing offers the possibility of using non-high toxic solvents and leads to nanostructured materials free of solvent contamination. After a brief overview of supercritical fluid properties and their use in the field of solid state chemistry and material science, we propose to describe the new process, developed in our laboratory, to synthesize nanostructured materials at different scale (100 Å - 10 μm) via self assembly of various metal, oxide or nitride nanoparticles. This process, based on a chemical transformation of an organometallic precursor inside a supercritical fluid, is a new route for obtaining nanostructured materials. This new route mainly deals with the dissolution of an organometallic precursor in a dense fluid, followed by a chemical transformation of the precursor and the formation of the nanostructured material in the supercritical fluid (high supersaturation are reached). The synthesis of nanostructured materials such as metals, oxides or nitrides is possible at clearly lower temperatures than those used in classical solid state chemistry route. Experimental results and simulations of our process show that it is possible to continuously adjust the building block and nanostructured material nature, size and morphology as a function of operating conditions. Today, massive production of nanostructured materials is one of the major limiting factor to their use. In these conditions, the development of a pilot facility of nanostructured material synthesis is in progress in our laboratory (100 g/h of powder).

3:45 PM P11.7
THE SYNTHESIS OF BUILDING BLOCKS FOR TEMPLATING SILICA VIA SELF ASSEMBLY: GOLD-SILICA NANOPARTICLES INCORPORATING A MERCAPTOSILANE CORE-SHELL INTERFACE. Michael Ming Yu Chen and Alexander Katz, University of California at Berkeley, Dept of Chemical Engineering, Berkeley, CA.

The synthesis of gold-silica core-shell nanoparticles via self-assembly is reported. These nanoparticles exploit the uniformity of colloidal gold and the strong interaction between thiols and gold to create a well-defined interface of functional group organization between the monodisperse gold cores and silica shell. The synthesis of the thiolate interface in these systems is accomplished indirectly relying on our recent discovery of thioester self-assembly on gold. We use a fluorescence-tagged thioester organosilane probe molecule to investigate the organization of thiolates on gold during the synthesis of the core-shell nanoparticle. The thioester probe binds to gold, undergoes sol-gel hydrolysis and condensation and subsequently deprotects to a thiol via gold-catalyzed thioester hydrolysis. This process results in a monolayer of condensed mercaptosilane on the nanoparticle surface without inducing colloidal instability, which was observed upon direct mercaptosilane addition at the same surface coverage. Binding experiments show a high packing density of thiolate comprising a footprint of approximately 25 Å² per molecule, and strongly suggest formation of a two-dimensional polysiloxane network on the nanoparticle surface at saturation coverage. Growth of a silica shell after mercaptosilane monolayer synthesis can be observed via transmission electron microscopy. The gold-silica core-shell nanoparticles are robust in that they can withstand organic solvent environments, as well as short-chain thiols, and maintain colloidal stability.

4:00 PM P11.8
PHOTONIC CRYSTALS SELF-ASSEMBLED FROM CORE-SHELL COLLOIDAL PARTICLES. Yu Lu, Yadong Yin, Younan Xia, University of Washington, Department of Chemistry, Seattle, WA.

This paper describes that gold nanoparticles and polymer particles have been coated with amorphous silica to form spherical colloids with a core-shell structure. The thickness of silica shells could be conveniently controlled in the range of tens to several hundred nanometers by changing the concentration of the sol-gel precursor or the coating time. These core-shell colloids could serve as the building blocks to fabricate photonic devices. In one demonstration, we showed that core-shell particles could be assembled into long-range ordered lattices (or photonic crystals) over large areas that exhibited optical properties different from those crystallized from silica colloids. In another demonstration, these core-shell colloids were assembled into chains of different configurations by templating against well-defined

channels patterned in thin films of photoresist. As suggested by previous studies, the plasmon coupling between gold cores makes these structures ideal candidates for nanoscale waveguides with lateral mode sizes well below the optical diffraction limit.

4:15 PM P11.9
CONTROLLING THE FORMAT OF BIOMOLECULAR CRYSTALS: FROM NANOCRYSTALS TO FILMS. Joshua Falkner, Mary E. Turner, Joan K. Bosworth, Vicki L. Colvin, Rice Univ, Dept of Chemistry, Houston, TX.

Protein crystals are useful tools in material chemistry. They allow one to create three-dimensional architecture on the nanoscale. Here we discuss methods for forming crystals useful for specific applications. Protein nanocrystals, for example, allow for the generation of high porous biomolecular substrates. Such systems provide fast diffusion rates and high accessibility in catalytic reactions. Another format of great interest is thin films. In this instance protein crystals are oriented specific with respect to an underlying surface and grow as large planar films. Methods for generating these crystal formats and their potential applications will be discussed.

4:30 PM P11.10
SYNTHESIS OF GOLD NANORODS/NANOWIRES AND THEIR GROWTH MECHANISM. Franklin Kim and Peidong Yang, University of California, Berkeley, Dept. of Chemistry, Berkeley, CA.

During recent years various methods have been developed to synthesize nanoparticles with controlled size and shape. Especially, one-dimensional (1D) systems such as nanorods, nanowires, and nanotubes are of much interest because their anisotropy produces a wide range of physical properties and assembly behaviors that are potentially useful for future applications. Numerous nanowires of semiconductors have been previously synthesized. However, there are relatively less studies done on nanorods/nanowires of metals such as gold and silver. Preparing nanowires of these metal is not trivial because their crystal structures are cubic, and isotropic structures are easily formed. Here, we present three different systems in preparing anisotropic gold structures; electrochemically synthesized gold nanorods with a diameter of around 10 nm and a controllable aspect ratio of 2 to 6, photochemically synthesized gold nanorods with similar diameter and aspect ratio, and gold nanowires prepared by hydrolysis with a diameter of 6 nm and a length of few microns. The reaction times are sufficiently long enough for time-resolved TEM studies to understand their growth mechanism. We were able to observe that rather than being an atom-by-atom growth on the nuclei surface, the reaction can go through an anisotropic aggregation of small nanoparticles to form gold wires as an intermediate state, which later dissociates into the final nanorods. For very slow reactions this intermediate phase is not observed, showing that this gold wire formation is kinetically controlled. Other interesting behaviors such as the control of aspect ratio with the addition of silver, and shape control with the surfactants will be discussed. By comparing these systems we are able to understand how anisotropic structures can evolve even from materials that have isotropic crystal structures, and also gain knowledge for better control in the size and shape of these nanoparticles.