SYMPOSIUM Q

Hybrid Organic-Inorganic Materials

April 1 – 5, 2002

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*Invited paper
SESSION Q1: WELL-DEFINED NANOBUILDING BLOCKS—PRECURSORS FOR HYBRIDS I
Chairs: Ulrich Schubert, P. Hubert Mohn and Brent Douglas View
Monday Afternoon, April 1, 2002
Metropolitan II (Argent)

1:25 PM OPENING REMARKS

Organic/inorganic nanocomposites are not only of great interest for potential applications, but also attractive as model systems for understanding the properties of new materials. This is because these systems can be designed to have specific properties and functionalities that are not achievable in either of the pure components. The development of such systems requires a deep understanding of the interactions between the organic and inorganic components, and the ability to control the structure and morphology of the resulting materials. This is where nanotechnology plays a crucial role, as it allows for the precise control of the size, shape, and composition of nanoparticles and nanowires.


Introduction: Our goal is to develop structure-property-processing relationships in nanocomposites prepared using functionalized silylalkoxoalkoxoalkylsiloxane (HSI) groups, to establish a complete understanding of the behavior of organic materials that are expected to offer physical properties nonlinearly related to the properties of the component materials. In the study described here, we have developed cubes with functionalized phenyl groups (RS = RSPh, RISPPh, NIPPhenyl, etc.). These materials provide access to high temperature nanocomposites, and can, in some instances, be melt processed and also offer access to materials with photonic and electronic as well as being discussed here.

References:

1:45 PM Q1.2 HYBRID INORGANIC/Organic Performance Fluids Based on Polymeric Silsesquioxanes (POSS). Rusty L. Blasko, Shawn W. Phillips, Brent View, Air Force Research Laboratory, Edwards AFB, CA; Justin Lebland, ERC Inc Edwards AFB, CA

Performance fluids that operate at high temperature can be useful for many applications including high efficiency automobile engines and jet turbines. One challenge in the increase of these fluids is to increase the use of the performance fluid while maintaining low temperature sensitivity. One possible solution to this problem is to combine the high temperature stability of a silsesquioxane fluid with the lubricity of hydrocarbons. Data will be presented on a wide variety of POSS alcohols that were synthesized to test the various POSS framework structures at higher temperatures. Thermal and viscosity data will also be discussed.

2:00 PM Q1.3 Molecular Design of Alkali Inorganic—Modified Sol-Gel Materials. Maki S. Ros and Bakul C. Dave, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL

This presentation will focus on the design, synthesis, and stimulation–response behavior of organically-modified silicates (ORMOHSs) containing responsive-active silanol units. The ORMOHSs behave as smart materials by undergoing structural changes at the molecular level to respond to changes in environmental variables. Typical responses shown by these glasses in the form of volume swelling/shrinkage to temperature, pH, salt concentration, and presence of organic molecules will be elucidated. Finally, applications of these glasses for selective intake and release, separation of different molecules will also be discussed.

SESSION Q2: STRATEGIES TO FUNCTIONAL LAMELLAR HYBRIDS MATERIALS
Chair: Jean-Francois Gerard and Pedro Gomez-Gomez
Monday Afternoon, April 1, 2002
Metropolitan II (Argent)

2:15 PM Q2.1 HYBRID RANDOM LASERS. M. Paylaki, D. Anglos, S.H. Anastasiadis, Institute of Electronic Structure & Laser, FORTH, GREECE; R.N. Boll and J.P. Ginnis, Department of MSE, Cornell University, Ithaca, NY

In conventional lasers photons are reflected back and forth through a cavity stimulated the emission of more photons helping to build up a stronger coherent radiation beam. A similar effect can be produced in a hybrid containing semiconductor particles. The recurrent scattering events may form closed loops providing coherent feedback. As a result, the light is scattered passing through the same grains, just as in an ordinary laser light bounces back and forth between the mirrors, leading to light amplification. In this paper we will describe our efforts to develop random lasers based on semiconductor nanoparticles (ZnS, TiO2) dispersed into a polymer matrix (epoxy, polyimide, PPV). The particles are the active centers providing both pumping (gain) and strong scattering whereas the polymer matrix provides better processability and mechanical robustness. The simplicity of the material system suggests relatively low costs for applications for lasers that can be potentially used in applications including micro-lasers, in search and rescue operations and in flat panel displays.

2:45 PM Q2.2 IN-SITU POLYMERIZATION VS IN-SITU INCORPORATION FOR THE NANOCOMPOSITE PSS/LDH. Flore Lecamp, El Montanya, Jean-Pierre Boeuf, Université Blaise Pascal, Aubière, FRANCE

With the ever-growing demand for multifunctional materials, nanocomposites present a great alternative compared to traditional systems. We present the incorporation of poly(styrene sulfonate) (PSS) between the sheets of layered double hydroxides. The incorporation of polymer between the galleries proceeds via different soft chemistry routes such as coprecipitation, in-situ polymerization, direct exchange, reconstruction or restacking. Using solid state 23C CP MAS spectroscopy, the in-situ polymerization of vinylbenzenesulfonate (VBS) is confirmed simultaneously by the disappearance of the C=C resonance peak and the presence of -(CH2)-. This reaction is associated with the contraction of the interlayer distance. It is worth noting the resonance peaks for the monomer are strongly shifted when present in the galleries of the LDH material (slightly depending on the carbon content), whereas they remain identical in the case of the polymer alone and when incorporated. Nanocomposites differ from each other by their morphology, their crystallinity, their surface area. Nitrogen sorption measurements indicate that the PSS incorporated material presents a pore size distribution ranging mostly in the mesoporous domain associated with a surface area of 60 m2/g, whereas these characteristics between the pristine LDH and PSS incorporated materials are not significantly changed. The distribution range in the mesoporous region associated with a surface area of 15 to 20 m2/g. This can be partly explained by the great difference in the first steps of reaction. Adsorption measurements show that the polymer intercalated material follows Freundlich type whereas they are of Langmuir type for VBS/LDH material. We demonstrate using 7Al solid state NMR that the in-situ polymerization method gives rise to material more stable in temperature than the other nanocomposite. The most stable 3D framework is obtained by the in-situ polymerization method.

3:30 PM Q2.3 Abstract Withdrawn.

3:45 PM Q2.4 IN SITU GROWTH OF ORGANICALLY-MODIFIED MAGNESIUM SILICATE CLAYS WITHIN POLY(ETHYLENE OXIDE) MATRICES TO PREPARE HYBRID LAMELLAR COMPOSITES. Bérénice Lebeau, Laboratoire de Matériaux Minéraux, ENSCMu, CNRS, Mulhouse, FRANCE; Nicola T. Whitton, Stephen Mann, School of Chemistry, University of Bristol, Bristol, UNITED KINGDOM

A direct synthetic method has been developed to produce hybrid materials composed of polymeric matrices infiltrated with layered inorganic particles. Amino-functionalised phospholipidic liposomes were prepared inside a poly(ethylene oxide) (PEO) matrix under quasi-anionic conditions. The sol-gel based method involved the precipitation of the silica-like framework from mixed ethylene/polymer solutions containing organotrisiloxane and metal salts. [3-aminopropyl]triethoxysilane [APTES] was employed to produce lamellar organically-modified magnesium silicate clays with structures analogous to the inorganic 2:1 phyllosilicates. Nanostructured PEO-liposome composites in bulk and films consisting of amino-functionalised magnesium organo-phyllosilicates embedded in PEO matrix have been prepared with different layered inorganic particle loadings. Typically, the molar ratio SiO2 (ethylene oxide unit) varied from 1:10 to 1:1. X-ray diffraction patterns showed for all samples showed reflections characteristic of crystalline PEO and layered magnesium organosilicate. The interlayer refinement at 2θ = 5.9° (diso, n = 1.561 ± 0.1 A) is characteristic of the 2:1 tricotahedral phyllosilicate structure and was observed in the XRD patterns in all the PEO-magnesium [organophyllosilicates synthesized. The presence of this reflection indicated not only the structural formation of the smectite-like structure, but also the ability of the layered inorganic framework to accommodate the presence of unreacted liposome and phospholipidic liposomes. The results of this study also open up new perspectives in the use of these composites as delivery systems, as they can be processed into any desired shape by compression or injection moulding.
the polymer matrix without losing long-range periodicity. Increasing the inorganic content of the samples resulted in an increase in the intensity of the reflections consistent with that of magnesium organo-phenylsilicates and a corresponding decrease in the intensities associated with reflections characteristic of crystalline PEO. The transparency of the hybrid films obtained indicated a high degree of interpenetration of both the inorganic and organic networks, and an inorganic domain size of nanometre dimensions.

4:00 PM Q2.5
MOLECULAR MODELING STUDIES OF ALUMINO-PHOSPHATE STRUCTURES. Parmjit Grewal, Paul Cox; Centre for Molecular Design, University of Portsmouth, UNITED KINGDOM; Julian Gale, Department of Chemistry, Imperial College of Science, London, UNITED KINGDOM; F. E. Wright, School of Chemistry, University of St. Andrews, Fife, UNITED KINGDOM.

The mixed organic-inorganic nature of the hybrid solids means that they present a notable challenge to theoretical methods because the unusual chemical environments adopted by some atoms make it difficult to derive reliable parameters for theoretical methods based on interatomic potentials. In this study, the aluminium-phosphate structures AlMePO, AlMePO(O), AlMePO, AlMePO-I and AlSiPO-II have been modelled using both semi-empirical quantum mechanical and Density Functional Theory (DFT) methodologies. These models have an advantage over molecular mechanics and related methods in that no parameters have to be derived for the particular structure under investigation. Semi-empirical calculations have also been used to investigate the barriers of rotation for the organic groups in relation to the framework. The energy minimised locations for the co-ordinates using both methods are found to be in excellent agreement with those reported in the literature, although the DFT approach produced better bond lengths in the important interface region. Useful information on the electronic distributions in these structures is also obtained, allowing us to determine charge interactions and to probe the nature of the H2O-framework interactions. This is exemplified by the results for AlMePO-II, which shows that although experimental determinations of the location of the benzyl groups is hindered by several factors, computational results strongly support the proposed structure for this material. The DFT approach has also been successfully applied in the determination of the structure of AlMePO-2. The values for the barrier to rotation for -(CH3) groups in the two structures investigated, AlMePO and AlMePO(O), are both consistent with rapid rotation of these groups at ambient temperature and compare favourably with the activation energy of -(CH3) groups in AlMePO determined via NMR measurements. In contrast, the barrier height for rotation of - (CH3) groups in AlMePO-I is calculated to be much higher, suggesting that motion of these groups will be significantly hindered even at elevated temperatures.

SESSION Q3: CHEMICAL STRATEGIES FOR THE DESIGN OF NEW HYBRIDS
Chair: Joel J.E. Moreno and Douglas A. Loy
Tuesday Morning, April 2, 2002
Metropolitan II (Argent)

8:30 AM #Q3.1
BUILDING HYBRID ORGANIC-INORGANIC MATERIALS USING SILSESQUIOXANES. Douglas A. Loy; Catalysis and Chemical Technologies Department, Sandia National Laboratories, Albuquerque, NM.

Control of porosity and chemical functionality are key capabilities in providing materials for catalysis, separations, and solid phase chemical synthesis. Great strides in engineering porosity have been made in materials such as crystalline zeolites and mesoporous, surfactant-templated materials that exhibit long-range order. However, the preparation of crystalline hybrid inorganic materials provides an alternative method for quickly constructing robust materials with controlled porosity and high levels of chemical functionality. For this presentation, I will review some of the recent advances in the sol-gel processing of hybrid organic-inorganic materials based on silsesquioxane building blocks. First, I will describe how simple organosiloxanes can be used to construct hybrid materials and discuss their advantages and limitations. The remainder of the presentation focuses on controlling porosity and functionality in hybrids based on bridged polysiloxanes. This will include a survey of synthetic methodologies, processing, properties and applications of these materials.

9:00 AM Q3.2
ORGANISATION IN ORGANOPOLYSILSESQUIOXANES PREPARED BY SOL-GEL PROCESS AND BY SOLID STATE POLYMERIZATION. Frédéric Ben, Bruno Beury, Robert Corru, Voilà Le Stréoc, Laboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Montpellier, FRANCE.

Organopoly-silsesquioxanes (NOPS) are silicon-bonded hybrid materials prepared by Sol-Gel process. Using precursors of the general formula R-Si(OEt)₃, a complete hydrosilylation/polycondensation lead ideally to cross-linked networks. This is currently under investigation for mesoporous material, NLO materials or luminescent materials for such organopoly-silsesquioxanes we have reported the presence of a short-range organisation leading to mesoscopic materials. By an alternative approach, performing hydrosilylation/polycondensation in the solid state of organo-poly(trichlorosiloxane), we have prepared organopoly-silsesquioxanes with a long-range organisation. We report on the short-range organisation of the organopoly-silsesquioxanes prepared by classical Sol-Gel process and the influence of the nature of the precursor (specially the connectivity at silicon) and the experimental parameters (solvent, catalyst, concentration). An intimate association during the chemical transformation and the mechanical orientations due to the cracks certainly play an important role. As a new alternative, we present the first results on the preparation of Organopoly-silsesquioxanes with various R groups by solvatonate hydrosilylation/polymerisation. Both evidences of chemical transformations and of the long-range organisation of the solid demonstrate the possibilities of this approach.

9:15 AM Q3.3
MODELS SYSTEMS FOR HYBRID ORGANIC-INORGANIC MATERIALS DEVELOPMENT. Thomas A.P. Steen, Institute of Materials Science, University of Connecticut Storrs, CT.

Development of new organic-inorganic hybrids can be facilitated by model systems that provide test beds novel materials combinations. Our research has focused on polymer synthesis from tethered initiators. Chain growth occurs from these initiating sites and provides a polymer layer comprising end-tethered macromolecules. In an effort to extend this concept to any inorganic surface we have initiated polymerizations from a variety of metal, oxide, sulfide and mesoporous surfaces. Our development strategy has focused on the preparation of stable nanoparticle surfaces for our initial studies. For particles with diameters ~2.50 nm we are able to utilize typical characterization tools of the organic chemistry to follow the progress of a sequence of reactions. With these tools in hand we have prepared hybrid metals, oxides, sulfides and mesoporous hydrocarbon polymers. These polymers include both flexible and semiflexible chains, sizeable liquid crystalline polymers and functional polymers. The utility of these polymers as precursors has been examined by infrared spectroscopy and the chemical compositions determined using NMR spectroscopy. These particle based model systems allow for determination of all aspects of the hybrid structure including particle diameter, surface area density of initiation sites, as well as polymer chain length and diversity.

9:30 AM Q3.4
AZOBENZENE BRIDGED POLYSILSESQUIOXANES. John T. Lee, Doug A. Loy; Catalysis and Chemical Technologies, Sandia National Laboratories, Albuquerque, NM.

Bridged polysiloxanes are a class of hybrid organic-inorganic materials that permit high levels of functionality to be incorporated into sol-gel processed monoliths or thin films. Because the organic group is an integral part of the network architecture that makes up the gel, there is an opportunity to explore the impact of photo-isomerization on the overall properties of the hybrid materials. In this study, an azobenzene bridged polysiloxanes monomer was prepared from dibromobenzene using the Pd(II) catalyzed Heck reaction. High yields were obtained with Pd(OAc)₂ and P(tol)₃ ligand. The photo and thermal characteristics of the monomer were determined with UV-vis, FT-IR, and NMR spectroscopies. The monomer was incorporated into both bulk and thin film hybrid organic'inorganic sol-gel gels where it is not only quantitatively and covalently bonded by two azobenzene groups. The azobenzene dyes geometric configuration may be controlled thermally or with light causing significant changes in the crosslinker. These materials were investigated to determine what effects the photoinduced thermal geometric isomerization of the azobenzene crosslinking moiety would have on the bulk physical and chemical properties of the materials.

9:45 AM Q5.5
METAL OXIDE-ORGANIC HYBRID MATERIALS BASED ON ORGANOPHOSPHORUS COUPLING AGENTS. P. Hubert Mustin, André Vieux, University of Montpellier II, Department of Chemistry, Montpellier, FRANCE.

Coupling molecules are required to bind covalently organic groups to an oxide network. Alkoxyalanes have been widely used for coupling with silica, but are much less efficient with metal oxides such as...
titanium. Organophosphorus compounds appear as valuable alternative coupling molecules: indeed, both P-C and P-O-C bonds are quite stable toward hydrolysis, and M-O-P linkages are chemically robust, as shown by the extraordinary variety of metal phosphonates reported in the literature. Moreover, M-O-P linkages are easily formed, for instance by non-hydrolytic condensations between M-OH (or M=OH) and POX [X = H, Me3Si, Et3Si] functions. These condensation reactions allow the preparation of organo-inorganic hybrids, either by sol-gel processing with metal alkoxide precursors or by modification of metal oxide surfaces. Phosphonate coupling molecules, BP(O)(O)x2, have been well characterized and extensively studied. In the sol-gel processing, the phosphonate precursors act as chemical modifiers, decreasing the reactivity of the metal alkoxide. Partial hydrolysis lead to polycyclic metal-organic hybrid microporous and homogenous naphthenophosphoryl metal phosphate and metal oxides, even under hydrothermal conditions. In the case of surface modification, the reaction of the coupling molecules involves not only condensation with surface hydroxyl groups, but also decomposition of the metal phosphonates, or even the formation of metal oxides such as titania, alumina, or zirconia.

SESSION QI: WELL-DEFINED NANOBUILDING BLOCKS-PRECURSOR MATERIALS FOR HYBRIDS II
Tuesday Morning, April 2, 2002
Metropolitan II (Argent)

10:30 AM Q4.1
CLUSTER-CROSSLINKED INORGANIC-ORGANIC HYBRID POLYMERS. Ulrich Schubert, Institute of Materials Chemistry, University of Technology, Vienna, AUSTRIA.

Metal oxide clusters capped by covalently bonded polymerizable organic groups are obtained by controlled hydrolysis of metal alkoxides in the presence of unsaturated carbonyl compounds. The cluster size and shape can be influenced by the reaction conditions. Radical polymerization of the unsaturated organic components of the clusters results in unsaturated organic hybrid polymers in which the clusters crosslink the polymer chains. The swelling behavior in organic solvents and the thermal and mechanical properties of the polymers are distinctly changed by incorporation of the functionalized clusters.

11:00 AM Q4.2
SYNTHETIC METHODOLOGIES FOR FORMING POSS MONOMERS FOR COPOLYMORIZATION INTO ORGANIC-INORGANIC HYBRIDS. Brent D. Viers, Rene Gonzalez, Timothy Huddad, Shawn Phillips, Air Force Research Laboratory, Pennsylvania Division and ERC Incorporated Edwards Air Force Base, CA.

Polyhedral Oligomeric Silsesquioxanes (POSS) are a novel class of inorganic monomers that can be copolymerized with commodity monomers (styrenes, acrylics, oxetans, etc.) to form organic-inorganic hybrid materials. Indeed, the synthetic control that is afforded during the POSS formation and subsequent functionalization allows for a variety of differing monomer architectures. We will discuss recent advances for the formation of POSS monomers, and show how the polymerization parameters are affected. It will be shown that simple steric hindrance assumptions do not always apply. Furthermore, there are now a wide variety of POSS-organic functionalities that are available, and the effect of different cores on the compatabilization of POSS into the matrix will be discussed.

11:30 AM Q4.3
CHAIN CONFORMATION IN LINEAR INORGANIC/ORGANIC HYBRID COPOLYMERS WITH SILSEQUIOXANE SIDE GROUPS. Christopher L. Sible, NIST Polymer Division, Gaithersburg, MD, Brent D. Viers, Air Force Research Laboratory, Edwards Air Force Base, CA.

Recently there have been efforts to create inorganic-organic hybrid materials by attaching POSS (polyhedral oligomeric silsesquioxanes) macromers to polymer chains as side groups. This scenario is attractive because the resultant hybrid is then soluble in a range of organic solvents. However, little is known about how the inorganic POSS affects the conformation of the polymer backbone. In bulk systems, there is often a strong tendency to form phase-separated domains of the inorganic component, especially at high POSS contents. Characterizing the simple chain conformational changes in random copolymers as a function of the POSS content in a dilute solution is one of the first steps to understanding the bulk structure of these hybrid materials. Specifically, we study the conformational properties of both poly(methyl-tert-butyldimethylsiloxane)-POSS (M-DSQ-POSS) and poly(dimethylsiloxane)-POSS (PDMS-POSS) random copolymers in dilute solutions as a function of POSS content. Small angle neutron scattering (SANS), using deuterated organic solvents, yields the conformation of the polymer backbone. These conformational properties are then correlated with the small angle X-ray scattering (SAXS) of the POSS units, which is easily obtained by small angle X-ray scattering (SAXS). Preliminary SAXS measurements indicate inter-scale correlations of both POSS and POSS (especially for high POSS contents) moieties even in the dilute solutions. This is discussed in terms of the possibility of forming POSS aggregates between several chains in the solution versus the simple spatial correlations that would be dictated by the connectivity in a single chain.

11:45 AM Q4.4
STRUCTURE CHARACTERIZATION OF ORGANIC-INORGANIC NANOCOMPOSITES FORMED BY THE SOL-GEL POLYMERIZATION. Libor Mareska, Institute of Macromolecular Chemistry, Academy of Sci of the Czech Republic, Prague, CZECH REPUBLIC.

Control of the structure evolution and proper structure characterization are crucial in developing perspective organic-inorganic (O-I) polymers. Of importance is also an interphase interaction supported by covalent bonding between phases, which is assured by using O-I precursors. We present a structure characterization of O-I networks and show the way of the structure control. We have prepared and followed build-up of O-I networks from two types of well defined O-I precursors: (a) alkoxyamine-endcapped oligomers that are crosslinked by sol-gel polymerization and (b) compact silsesquioxane (SSQO) clusters with epoxy functionalities forming a network by reaction with oligomeric dimines. In either case, the network junctions are created by the SSQO domains. The domains were analyzed and as the network structure analysis is difficult we used also model systems easy to characterize. (a) The SSQO junction in the networks from endcapped oligomers is mainly composed of polyhedral cage structures. NMR analysis reveals an agreement between the network and the model. Solgel polymerization of model organoalkoxysilane with a long organic substituent results in formation of an octamer cage. The intramolecular condensation preventing gelation of the system is preferred and the tendency to cyclization increases with the length of the organic chain. (b) In the second system the SSQO domains are synthesized first by the sol-gel polymerization of [3-glycidoxypropyl]trimethoxysilane and characterized. Under proper catalysis, stable clusters corresponding to the octamer cage and larger cage-like structures containing epoxy functionalities are formed. These were interconnected with dimines to form a network. Structure evolution during network formation, microphase separation and gelation were followed using SAXS and DSC. Mechanical properties and interphase interaction of the cured networks of both types were compared and structure-properties relationships were determined.

Acknowledgement
The author acknowledges support of the Grant Agency of the Academy of Sciences of the Czech Republic (no A405088).

SESSION Q5: BIOMATERIALS, BIOGELS, BIOMIMETIC APPROACHES TO MATERIALS
Chair: Carole C. Perry, Daniel E. More, Bruce S. Dunn and Jeffrey I. Zink
Tuesday Afternoon, April 2, 2002
Metropolitan II (Argent)

1:30 PM Q5.1
A STATISTICAL APPROACH TO THE EFFECT OF SOL-GEL PROCESS VARIABLES ON THE PHYSICAL PROPERTIES OF POLYMER-SILICA HYBRID MATERIALS FOR USE AS BIOMATERIALS. Carole C. Perry, David Egin, Department of Chemistry and Physics, The Nottingham Trent University, Nottingham, UNITED KINGDOM, Sadia Ali, Sandra Downes, Group Research Centre, Smith and Nephew Plc, York, UNITED KINGDOM.

Hybrid polymer-silica materials for potential use in orthopaedic applications have been prepared using an experimental design approach to investigate the effect of synthesis variables separately and together on the physical form of the organic polymer. The five factors investigated were the molar ratios of tetraethoxysilane (TEOS)/polymer, EtOH/TEOS, THF/TEOS, water/TEOS and catalyst (HCl)/TEOS. The maximum and minimum levels for these variables were selected using literature data [1]. All other synthesis conditions were kept constant. A combination of DSC, XRD and

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FTIR methods were used to obtain information on the arrangement of the organic polymer in the hybrid materials. A measure of the relative crystallinity originates from polymer crystal phase and depends on information on the incorporation of the organic polymer within the silica network. The lower the value of the relative crystallinity index, the greater the extent of mixing of the two phases. The three analysis techniques gave similar information. In accordance with other studies [2,5] increases the molar ratio of TEOs/polymer lead to increasing incorporation of the organic polymer into the silica network. Incorporation of the organic polymer also increased with increasing HCl/TEOS ratio. As our studies show, the effect of acidic concentration on the silicate network was simultaneous, so it was possible to identify, for the first time, that an increase in catalyst (HCl) concentration affects the condensation of TEOs in the sol-gel material rather than the hydrolysis rate (for the set of conditions investigated) and that in turn affects the ability of the organic polymer and silica phase to form interpenetrating networks, an important requirement for the generation of a potential hybrid polymer-silica biomaterial for orthopedic applications.

References:

200 P M Q5.2
ASSOCIATION OF SILICA WITH BIOPOLYMERS FOR THE DESIGN OF NEW BIOMATERIALS Thibaud Corain, Marie-Madeleine Giraud-Guelle, Clement Sanchez, Jacques Livage, Chaine de la Matiere Condenser, Universite Paris VI, Paris, FRANCE.

This paper is devoted to our recent investigations of the biopolymer/silica interface. These studies aim at getting a better understanding of the interactions between biomolecules and silica precursors used to design new bio-inspired materials. Our strategy lies in the association of silica precursors with biopolymers presenting gelation properties. Alginate acid, a natural polysaccharide, was chosen because of its common use as a host matrix for cell immobilization. We have formed a silica gel in the presence of the polymer. Gelation of the trapped alginate could be consequently performed by addition of a divalent metal cation. The morphological features of the composites related to depend on the biopolymer content of the initial solution. The association of alginate and silica was also used to obtain new nanocomposites coated with a sodium silicate solution, leading to improved mechanical properties while maintaining selective diffusion of the outer membrane. In a second step, we have tried to prepare mixed silica-collagen gels. Silica precursors and collagen solutions were mixed in acidic media and simultaneous gelation of both components was induced by ammonium vapour diffusion. Influence of synthesis parameters on silica morphology and collagen organization will be presented.

2:15 P M Q5.3
SYNTHESIS, CHARACTERIZATION AND IN-VITRO RELEASE OF GENTAMICIN FROM CAROLINE HYDROXYAPATITE ACRYLATE GRAFTED ONTO POLY[(MMA-GMA) FUNCTIONAL MICROSOURCES FOR OSTEOGENIC AND BONE FILLING MATERIALS. M. S. Sohikumar, K. Prabhakar Rao, Department of MS&E, University of Florida, Gainesville, FL.

Many efforts have been made towards the development of new bone substitute materials. Hydroxyapatite (HAP)/functionality polymer composites have attracted much attention since such composites have some unique advantages over their conventional corresponding components. Poly(methyl methacrylate) [PMMA] and its derivatives as an adhesive in bone orthopedic applications is well known. In the present paper, attempts were made to prepare hydroxyapatite and epoxy containing PMMA functional [PMMA-F] microspheres using chain transfer agent, mercaptopropanol and glycidyl methacrylate. These PMMA-F microspheres were prepared by dispersion polymerization technique and the coralline hydroxyapatite [CHA] was synthesized using acryloyl chloride. These prepared CHA was grafted onto PMMA-F microspheres by polymerization initiation techniques. These grafted ceramic-polymeric composites were characterized by various techniques such as XRD, FT-IR, TGA, DSC, and EDX. These functional microspheres and grafted microspheres were analyzed for particle size distribution using particle size analyser and found to be 200 microns and 300 microns respectively. The optical and SEM micrographs clearly indicated that the CHA was grafted onto the PMMA-F microspheres. Gentamicin was coupled to the grafted microspheres and in its in-vitro release was carried out at a temperature of 37 °C. It is normal to use these biomaterials in orthopedics particularly in the repair and regeneration of bone and dental.

2:30 P M Q5.4

Synthetic materials with ordered multidimensional pore systems of micro-, meso-, and macroporous scales have not been successfully accomplished even though considerable effort by temperature-programmed hydrothermal treatments and sol-gel processes. Such materials are of considerable interest for providing easier mass transport to the active sites and improving reaction efficiencies. Here we report the synthesis of ordered ceramic materials with hierarchy produced by in-situ mineralization of ordered wood-cellular structures with surfactant-templated solgel at different pHs. At low pH, a silicic acid is casted onto inner surface of wood cellular structure and it penetrates into pores left, where degraded lignin and hemicellullose are leached out, to form a positive replica, while at high pH the precipitating silica particles due to fast condensation clog the cell and pit structures to form a negative replica of wood, regardless of fast leaching of lignin and hemicellulose. The calcined monoliths produced in different pHs contain ordered wood-wall structures, multi-layered cell wall, pits, vessels well-preserved with positive or negative contrasts, respectively. The surfactant-templated mineralization produces ordered hexagonal monoliths with 20A in the cell walls after calcination. Such monolithic metal oxides have great potential in catalysis, separation, bioengineering with a great improvement.

2:45 P M Q5.5
CRYSTALLIZATION OF L-ARGININE PHOSPHATE (LAP) MICROCRYSTALS IN A SILICA SOL-GEL MATRIX. Tatyana A. Faltens and Bruce Dunn, Univ of California Los Angeles, Materials Science and Engineering, Los Angeles, CA.

The relationship between crystallization and gelation in a system consisting of an organic non-linear optical crystal in an inorganic sol-gel matrix was studied. AC impedance measurements were used to determine the solubility of LAP in sol-gel as a function of temperature, the induction times for crystallization of LAP in sol-gel as functions of both temperature and concentration, and the overall rate of LAP precipitation. The solubility of LAP in sol-gel follow exponential behavior with an enthalpy of solution of 0.88 eV, which is comparable to that measured for the solubility of LAP in water. The primary difference between solubility of LAP in sol-gel and water is in the pre-exponential factor, which is about 8 times smaller than that in water. The induction times for crystallization were used along with the precipitation rates and observation of the final crystal morphology, size and number density to elucidate the nucleation and growth mechanisms operating over a range of experimental supersaturation and gelation temperature. This information was used to create a phase map for the crystal growth and gelation. The phase map shows that regions where crystallization occurred primarily before the gel had become fairly well formed with regions of homogeneous nucleation while crystallization that occurred after gelation was heterogeneous. The phase map also shows regions with different preferred growth mechanisms that depend primarily on the instantaneous supersaturation.

3:15 P M Q5.6
SILICON BIOTECHNOLOGY OFFERS NEW PATHS FOR STRUCTURE-DIRECTED POLYMERIZATION OF SILICA AND SILsesQUOXANES. Daniel E. Morse, Jennifer N. Cha, Katsumiko Shimizu, Yan Zhou, Jiuxing Guo, Jan Sumerel, Galen D. Stucky and Bradley F. Chmelka, University of California at Santa Barbara, Materials Research Laboratory, Santa Barbara, CA.

Biological systems fabricate 3-dimensionally organized silicified composites at low temperatures and near-neutral pH, with a precision that is presently far beyond our human capabilities. Analyses of the proteins, genes and molecular mechanisms governing the formation of these composites revealed an unexpected mechanism of synthesis with potential industrial applicability. We found that the silica needles made by a marine sponge are hybrid materials. Each contain an occluded axial filament of protein composed of repeating assemblies of three similar subunits we named "silicens." Analysis of the purified protein subunits and the cloned silicin DNA revealed that at least one gene is associated with a family of hydrolytic enzymes. From this prediction, we discovered that the silicin-enriched proteins can form and spatially direct polymerization to form silica, phenyl- and methyl-silsesquioxane from the corresponding silicon precursors at neutral pH and low temperature. Catalytic activity also is exhibited by the silicin subunits obtained by dissociation of the protein filaments, and those produced from recombinant DNA templates cloned in bacteria. Genetic engineering was used to produce variants of the silicin.
molecules with substitutions of specific amino acid sidechains. In conjunction with molecular modeling, this allowed us to probe the determinative activity with confidence and identify the specificity of the amino acid sidechains required for hydrolysis of the silicon alkoxides.

From these findings, we then predictively synthesized biomimetic diblock copolymer incorporations of the essential features found to be required for catalysis.

As predicted, these self-assembling synthetics mimic the activities of the native silicateins, catalyzing the polymerization of siloxanes at neutral pH, while simultaneously directing the 3-dimensional structures of the resulting silicon-based composites. We now use exploratory activity and confirm the identification of the silicateins and their biomimetics to produce ordered polyunsaturates and inorganic/organic hybrid materials with enhanced optical and other physical properties, and to write nano郑kstructured features of silica on silicon chips.

3:45 PM Q5.7

BIOL aerally-DRIVEN FABRICATION OF A HYBRID ORGANIC/INORGANIC DEVICE. Rajesh R. Naik, Lawrence L. Brodt, Sue M. Kirkpatrick and Morley G. Stone. Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Dayton, OH.

The ability to direct the assembly of nanostructured components into functional structures is one of the major goals of biomimetic approaches. In order to fabricate a highly ordered organic/inorganic hybrid structure, we combined the self-assembling activity of peptides with a holographic two-photon induced photopolymerization process. The R5 peptide, isolated from the dinactin Cylindrotheca fusiformis, forms silica nanoparticles from silicate anions at physiological concentrations in vitro. By incorporating these nanoparticles to a monomer formulation, peptide-rich regions can be created on the polymer surface using the holographic two-photon induced photopolymerization process. After exposing the cured polymer to a silica precursor, silica nanoparticles are precipitated in the peptide-rich regions resulting in a highly ordered two-dimensional array of silica nanoparticles on the polymer backing. The diffraction efficiency of these devices increases nearly fifty-fold when compared to a polymer hologram without the silica spheres. This is the first demonstration of the use of peptides in biologically driven synthesis and assembly of silica into a functional optical device.

4:00 PM Q5.8

DEVELOPMENT OF POROUS POLYMERIC-CERAMIC COMPOSITES AS BONE GRAFTS. Samir Kallie, John Finkie, Sasuin Bose, Howard Honick and Amir Bandyopadhyay, School of Mechanical and Materials Engineering, #School of Molecular Biosciences, Washington State University, Pullman, WA.

Biomaterials have made significant contributions to the advancement of modern health care and drug delivery industries. An ideal bone graft should have high strength and toughness as well as interconnected porosity for tissue ingrowth. The present research is based on development of polymer-ceramic composite (PEP) using polycaprolactone (PCL) ceramic for bone graft applications. Controlled interconnected porosity composite scaffolds were fabricated using a fused deposition modeling (FDM) system, a commercially available rapid prototyping (RP) process. Porous scaffolds were characterized for their physical, mechanical and biological properties. First, ceramic and polymer materials were mixed under shear using a rotor rheometer. Compounded materials were then extruded at a 1.78 mm diameter filament using a single screw extruder. These filaments were used as a feedstock material for a FDM 1650 machine for direct fabrication of controlled porosity parts. Tensile properties of the as processed composites were measured on dog-bone samples. Uniaxial compression tests were performed on cylindrical porous samples. It was found that as processed samples with 200 micron average pore size having ~13 volume% porosity show an average compressive strength of 10 MPa. Cytotoxicity and cell proliferation studies were conducted with modified human osteoblast cell line (OEC-1). These samples are non-toxic and show excellent cell attachment during the first two weeks of the study. The presentation will describe processing, characterization, and in vivo studies of PPE-CP composites having controlled three dimensionally interconnected porosity.

SESSION Q6: POSTER SESSION HYBRID ORGANIC/INORGANIC MATERIALS

Tuesday Evening, April 2, 2002

8:00 PM

Metropolitan Ballroom (Argent)

Q6.1

Transferred to Q4.4.

Q6.2

DESIGN AND SYNTHESIS OF NANO-POROUS FRAMEWORK POLYMERS. Rick Y. Lu, Amy M. Babb, Vaughan Schrader, Joe Macias, Wilfredo A. Fernandez, Edward E. Kohler and Benjamin J. Biel, Department of Chemistry, University of Houston-Clear Lake, Houston, TX.


Q6.3

OXOTANTALUM CLUSTERS AS BUILDING BLOCKS FOR INORGANIC/ORGANIC HYBRID MATERIALS. Silvia Gross, Guido Kiesewetter, Ulrich Schulz and Istvan Mucsko-Cherino. University of Tech, Vienna, AUSTRIA, Vito Di Noto, Dept of Inorganic Chemistry, Univ. of Padova, Padova, ITALY.

Novel organically modified tannakum oxide clusters were prepared via the sol-gel route by reaction of tannakum pentaoxide with acrylic or methacrylic acid. The clusters, bearing polymerizable methacrylate moieties, were then polymerized with methacrylacte or styrene as copolymers. In the resulting inorganic-organic hybrid polymers the clusters crosslink the polymer chains very efficiently. Radical free polymerization was performed by varying the monomer to cluster ratio. The physical properties and structural features of the hybrid polymers were investigated by the swelling behavior, small angle X-ray scattering (SAXS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Raman spectroscopy, infrared spectroscopy (IR), 13C MAS NMR and impedance (EIS). Hybrid polymers doped with only 0.5-2 mol% of the functionalized clusters show an impressive chemical stability and good mechanical properties. Moreover, they display improved thermal stability; their decomposition stage is shifted to higher temperatures with respect to the undoped polymers. The tannakum cluster based hybrid polymers are very promising dielectric materials owing to the fact that their conductivity are five order of magnitude lower than that of pristine PMMA.

Q6.4

MULTIFUNCTIONAL MATERIALS: 3D CONFINED ELECTRONICALLY CONDUCTIVE POLYMERS INTO LDH MATRIX. El-Mosta Moulaied, Marc Bouhlel, Fabrice Lerouge, Jean-Pierre Besse, Dept of Chemistry, Univ. Blaise Pascal, Aubiere, FRANCE.

A great interest has been devoted to the preparation of multifunctional materials based on topotactic reaction with a 2D host structure. For instance, this is illustrated by the system polyacrylamide [PAM]@2D material. In these organic/inorganic materials, the polymer is incorporated to enhance the electronic conductivity, the dimensional dimension provides the stability and the processability. Aniline-sulfonate is readily incorporated between the layers of [Mg(6)Al]6(OH)16 hydrakite type material. As a result of this polymerization of the monomer, there is an increase of the basal spacing, indicative of a confined environment for the polymer. The presence of sulfonate polyaniline [SPAN] under its conductive state is verified by FTIR. Additionally, in situ ESR measurements are carried out in temperature to better understand the polymerization process. Both techniques indicate the
presence of short oligomers for which the conduction can be explained by a polaron transverse mode (narrow T-dependant signal, \( \Delta H_{\text{pol}} \approx 26 \text{G} \) (293K) associated with \( g = 2.0013 \)). Direct exchange of (SPANI), prepared chemically by sulfonation of the desired polymer, is carried out. We discuss the behavior of the material in comparison with the simple model made by the in-situ polymerization method. Finally, the electrochemical behavior in ionic liquid was presented for the hybrid materials (monomer or polymer/LDH), associated with ESR measurements at different voltage steps. The ESR linewidth for the broad signal characteristic of the LDH framework is found to be independent of the electrochemical treatment (\( \Delta H_{\text{pol}} \approx 1000-1100 \text{ G} \) with \( g = 2.0172 \)), whereas it is significantly changed between the oxidation (20mV/Pt) and the reduction (-120mV/Pt).

Q6.5
Transferred to Q10.7.

Q6.6
TIN-BASED HYBRID MATERIALS PRECURSORS OF MESOPOROUS TIN OXIDE. Bernhard Joussen, Horace Bregier, Thierry Toupance, Laboratoire de Chimie Organique et Organometallique, Université de Lorraine, France; Mohamed Laourine, Département de chimie, Université Cadi Ayyad, Marrakech, Morocco.

Doped or undoped tin dioxide has numerous applications as catalyst or sensor which requires high specific area and defined porosity for a better efficiency. Hybrid materials have recently attracted much interest for the preparation of materials with tailored morphologies and properties. This is why we prepared tin-based hybrid materials and used them as precursors of tin oxide. Here, we report the formation of a new class of bridged trialkyaminane leading to gels upon hydrolysis. The starting materials were obtained by alkynylation of the corresponding bridged trichloroamines, where the tms are linked through two alkyl, aryl or hengly spacer. The bridging aromatic ligand is the spacer that insures that organic network polymers are formed and that the organic moiety is homogeneously distributed at the molecular level. Transparent gels were obtained depending on the nature of the spacer and the bridging condition. Then, the gels were calcined at 400 °C thermolysed to give micro- or mesoporous tin oxide with high specific area.

Q6.7
MESO-ORDERED SILICA FILMS FORMED BY SUGAR-BASED SURFACANTS. Urska Lawrence, Steiger, Nicola H. Haining, Technische Univ Wien, Inst für Anorganische Chemie, Wien, Austria.

Sugars-based amphiphilic molecules that carry a chiral information in their carbohydrate head group are used as templates in the sol-gel processing of thin silica films. The films are produced by the dip-coating technique in a humidity controlled chamber. Different surfactant systems, such as alkoxysilanes and alkyl glycosides (e.g. n-octyl(\( \beta \)-D-glucopyranoside, n-octyl \( \beta \)-D-galactopyranoside and n-dodecyl \( \beta \)-D-maltopyranoside), were compared with respect to their ability to organize into mesoporous silica films. The larger polar head group (malto) decreases the critical packing parameter and thus beneficially influences the formation of a favourable hexagonal phase over the lamellar phase, which is formed with a glucopyranoside head group. The meso-icratic silica films show a strong influence of the humidity during their synthesis. For non-structured films, ordering could be achieved by exposing the as-deposited films to a high humidity for several hours. In addition to commercially available glycol-silane surfactants with alkyl hydrophobic units, some novel-made glycol-silane surfactants with poly(dimethylsiloxane) hydrophilic units are suitable for the synthesis of ordered silica films. As a silica source, the prehydrolyzed tetramethoxysilane in an acidic alcoholic solution is used. The investigation of the chiral imprints on the silica pore walls is visualized in the future work.

Q6.8
ORGANIC-INORGANIC HYBRID MATERIALS FOR DILUENT NON-DETOXINAL COMPOSITES. Simone Kleindorfer, Norbert Strunz, Thomas Völk, Volker Rheinberger, Tochter Vivant AG, Schaan, Liechtenstein.

Organic-inorganic hybrid materials based on functionalized silanes are being used for dent fillings, because of their good mechanical properties, low volume shrinkage and improved corrosion resistance. Unfortunately, such filling materials still contain methacrylates as the diluent. Diluent-free composites could be produced by using low-viscous sol-gel components. Low-viscous sol resins were formed by hydrolysis and condensation of new dimethacrylate-triolignosulfonates with an amine spacer in the presence of ammonium fluoride. The novel siloxanes were synthesized by Michael addition of the corresponding acryloyloxyalkyl methacrylates with 3-aminopropyl-triethoxysilane (APTES). Furthermore, the reaction of APTES with the addition product of sucrose or glucose anhydride with glycidyl dimethacrylate resulted in new dimethacrylate-functional oligomeric siloxanes. Hydrolysis and condensation of these siloxanes were carried out in the presence of 0.5 N HCl and have been studied by \( ^{1}H \) NMR spectroscopy. Diluent-free composites have been obtained by photopolymerization of the polycondensates and their mixtures in the presence of camphorquinone and ethyl \( \beta \)-(dimethylamino)benezene with visible light. Further improvement of the mechanical properties of the polycondensates was obtained by incorporation of dispersed SiO\textsubscript{2}-taurogostepes and well dispersed green copper(II) ions in methacrylate groups. With a cured composite containing 19 wt% of the reinforced polycondensate mixture, 80 wt% inorganic filler and 1 wt% of photoinitiator a flexural strength of 112 MPa and a modulus of elasticity of 18000 MPa were obtained.

Q6.9
HELICAL LIPID - SILICA MESOSTRUCTURES. Allison Seddon, Christine Spickerman, Stephen Mann, University of Bristol, School of Chemistry, Bristol, United Kingdom.

Helical ribbons and cylindrical tubules formed by self-assembly of chiral amphiphilic molecules have attracted much research interest. In particular, the tubules formed from synthetic lipids such as dicycloxyphosphoryl chloride have been extensively studied as they provide a valuable insight into molecular self-assembly. In this work, dicycloxyphosphoryl chloride tubules have been mineralised with amorphous silica. The tubules were also formed in-situ during silica hydrolysis/condensation reactions to form a twisted lamellar silica-lipid mesophase. The helical structures show interesting photoluminescence properties, turning blue due to enyne polymerization of the lipid dicycloxyphosphoryl backbone. Significantly, this behaviour is not observed when premineralised tubules are placed in the reaction medium, suggesting that the presence of inorganic silica within the in-situ coated tubules is required. The mineralised tubules were studied by electron microscopy, powder x-ray diffraction, IR, diffused reflectance UV/Vis and Raman spectroscopy.

Q6.10

New poly(methylphenylsiloxanes) (PMPs) with highly regulated structure were synthesized with organic flexible polymers. Nano-sized surface images of these hybrids are observed by Atomic force microscopy (AFM). The prepared pure PMPS spin-coated film and PMPS/organic flexible polymer systems showed excellent transparency and good film planarity. The distribution of organic domains in the inorganic matrix showed homogeneous regularity and the size of dispersed phase was as small as ten of nanometers. No self-aggregation of each phase occurred in the range of organic portion from 10 to 30 wt%. As interaction such as interhydroxyl and aromatic-aromatic interaction increases, more uniform phase distribution and smaller domain size on continuous inorganic matrix are achieved. The effects of interactions were evaluated by FT-IR, which results showed good agreement with AFM measurement. In addition, temperature-dependent dielectric properties of the hybrid thin films were investigated. Other physical properties and characterization of the hybrid system will be discussed in the conference.

Q6.11

Inorganic/organic hybridization has greatly attracted scientific and industrial interests. The organo-dispersed inorganic matrix would be applied to insulator and electronic industries such as microelectronic packaging materials, optical devices, liquid crystal display elements, magnetic recording media, and cardiological drugs. We synthesized poly(methylphenylsiloxanes) (PMSQ) and Poly-DL-lactic acid or PDLLA-PDL-lactic acid (PDLLA-PDL-lactic acid, 1:6, hexamethyle) Prepared inorganic/organic hybrids are investigated in terms of nano-sized morphology by atomic force microscopy (AFM). In particular, the inorganic/organic hybrid material based on polyorganosiloxanes (PSQ) is one of the most promising candidates for low K materials. The hybrids exhibited excellent film constance, adhesion, and planarity. Nanofoming process carried out at optimized condition. The nanofomeded PMSQ thin films were studied by morphologies and
dielectric properties. As increase of PDLA-L(-)+b-meliod resulting air-oxid, dielectric constants of the films were significantly lowered. Particularly, in the case of P(1-MPS) /PDLA-L(-)+b-meliod (85/15) hybrid films shown not only the most uniform nanofon distribution but also the best structural stability among the prepared thin films.

Q6.12 IMMOBILIZATION OF PHOSPHINES ON METAL OXIDES USING PHOSPHONATE COUPLING AGENTS. P. Hubert Martin, Gilles Guerrero, André Vieux, CNRS-University, Montpellier, FRANCE.

The preparation of organic-inorganic hybrid heterogeneous catalysts is an important application of trialkoxysilane coupling agents. As phosphines form stable complexes with a great variety of transition metal oxides, phosphines such as 

Ph3P(=CH2)2Si(OEt)2

have been extensively used to immobilize phosphines on silica supports. On the other hand, it was recently shown that in practice these coupling molecules cannot be used with other oxide supports, such as TiO2 and MgO [1]. We report on the study of phosphonophosphines compounds as coupling molecules. These molecules appear complementary of alkoxysilanes and they are well suited to the preparation of covalent TiO2-based hybrid materials by sol-gel processing [2] or surface modification [3]. In this paper we report the solgel immobilization of phosphines and their Pd and Pt complexes in TiO2 and ZrO2 matrices, using 

Ph3P(=CH2)2Si(OEt)2

and 

Ph3P(=P(=O)(OSiMe)3)2

 coupling agents. The hybrid solids were characterized by elemental analysis, solid-state MAS-NMR spectroscopy, surface area measurements, XRD, and complexation-decomplexation experiments.


Q6.13 SOLUBLE METHANOFULLERENES AND FULLERENEDRUMS IN SOL- GEL MESOPOROUS SILICA HOST MATRICES FOR REVERSE SATURABLE OPTICAL ABSORPTION. D. Felder, J.F. Nerengartzen, B. Heinecke, Institute de Physique et Chimie des Matériaux de Strasbourg, Strasbourg, FRANCE; G. Kopitkov, Institut of Materials Science and Applied Research, Vilnius University, Lithuania; A. Chaikov, Ioffe Physical-Technical Institute, St. Petersburg, RUSSIA.

The non-linear optical properties of the fullerene C60 have been extensively studied because of its spectrally broad absorption and its fast non-linear response in the Reverse Saturable Absorption process. The use of C60 embedded solid porous matrices presents a number of advantages as excellent optical quality and mechanical stability. The poor solubility of pure C60 limits, however, the optical density that can be reached. We study two ways to increase the content of light limiting compound: to increase the pore amount and size and to synthesize highly soluble compounds. The mesoporous silica host matrices are prepared by following a TMOS acidic hydrolysis formamide. Several parameters ruling the pore size were investigated. After a heat-treatment at 600°C the pore size is defined by nitrogen physisorption. A wide range of mesoporous samples is obtained (pore sizes from 24 nm). The relationship between composition and pore size is given. AFM measurements give evidence that the porosity is related to intergrain voids of nanoscale silica particles. On another hand we synthesized new methanofullerenes and fullerenedrums with peripherial triethylene glycol chains. The preparation scheme can be described. The methanofullerenes are dissolved in THF-Water-Ammonia solutions and added to the sol before gelation. The fullerenedrums are infiltrated into mesoporous silica using soaking procedure followed by drying at 40°C. We study and compare the limiting dynamics of several samples by single and double pump-probe experiments. For methanofullerenes in silica, a shortening of the single-shot lifetime is observed compared to C60 in solution. This is attributed to a larger aggregate size and to the shortening of the single-shot lifetime by solid-state effects. Concerning fullerenedrums they show a similar single-shot cross section and single shot lifetime, but a quantum efficiency (single to triplet). Their properties let us think that they can be of high interest for optical protective coating.


Using surfactant-mediated synthesis, a large variety of organic functions can be incorporated in silica-based organosilicon materials in order to create original materials that can find applications in fields ranging from adsorption, ion exchange, catalysis and sensing technologies. The organic functions are usually introduced during the synthesis of the templated network, either in pendent or bridging groups using two families of organosilanes, [RSi(OEt)3] and [OESi2]-2SiR-OESi[OEt]2 respectively. Various functionalized and hydrophobic silica materials have been synthesized introducing alkyl or aryl moieties bonded to Si using met-hydroxytriethoxysilane, bis(triethoxysilyl)ethene phenyltriethoxysilane, 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 1,2-bis(triethoxysilyl)benzene in the presence of octyltrimethyl ammonium bromide. Their detailed structural characterization have been performed by means of XRD with synchrotron radiation, one and two-dimensional nuclear magnetic resonance spectroscopy and adsorption-desorption experiments. Then the synthesis was extended to dip-coated thin films using evaporation induced self-assembly.

Q6.15 INDUCED MECILLIZATION OF HYDROPHILIC DILOCK COPOLYMERS. Corine Gerardin, CNRS-Ecole Nationale Superieure de Chimie, Montpellier, FRANCE; Martin In, Université Montpellier II, Montpellier, FRANCE; Mathieu Jomard, CNRS Rhône Complex Fluids Laboratory, Cranbury, NJ.

New hybrid aggregates were prepared and were shown to be efficient precursors of organic-inorganic particles. They form by self-assembly of hydrophilic block copolymers in the presence of small inorganic entities in water. The block copolymers are water soluble and contain two blocks with separated functionalities. One block is neutral, such as polycrylamide (PAM) and the other is charged, such as sodium polystyrene sulfonate (PAH). The particles selfassemble in the presence of positively charged inorganic species due to complexion of the inorganic ions by the neutral block. Mixing PAH and PAM copolymers with aluminum and copper salts, we have shown that well-defined aggregates form. Small cationic entities are preferred for the aggregate formation, such as the salts of Al3+, Cu2+, or polyatomic clusters such as Al138+ and Al148+. The micelle-like aggregates were extensively characterized. Sizes were estimated by light scattering and small angle neutron scattering (SANS); hydrodynamic diameters together with radii of gyration were determined. Form factors of the aggregates were obtained by SANS. It was shown that, for some specific relative block lengths, spherical starflattened objects formed. The core of the object is constituted by the complex and the neutral polystyrene block forms the diffused corona. Zeta potentials were measured as a function of the polymer to metal ratio in order to follow the aggregate formation. The influence of the following parameters was also studied: the polymer molecular weight and block lengths, the number of complexing functions per metal ion and the pH of the solutions. Finally, the aggregates have been shown to be adjustable precursors for the formation of colloidal suspensions of metal hydrolysis products.

Q6.16 BIOMIMETIC SYNTHESIS OF SILVER NANOPARTICLES. Rajesh Naik, S. Stringer, Sharon Jones & Merky O. Stone, Materials and Manufacturing Directorate, Biotechnology Group, Air Force Research Laboratories, Wright-Patterson AFB, OH.

The fabrication of nanoscale materials for potential use in creating advanced functional structures has lead to the development of a number of different innovative approaches, especially the use of a biomimetic approach. In contrast to harsh traditional material synthesis techniques, biomimetic approaches offer an alternate benign or "green" route for nanoscale material fabrication. Many biological systems are capable of synthesizing nanoparticles from inorganic materials such as silica, silver and ferric oxide. Isolation of the organic molecules involved in these processes may facilitate the creation of hybrid materials. Phage display, a commonly used method for screening combinatorial libraries of peptides, is a selection technique in which peptides are displayed on the surface of a high coat protein resulting in the display of the fused protein on the surface of the phage particle. Using combinatorial approaches, we were able to isolate peptide sequences that bound specifically to silver. More importantly, we show that some of the phage particles display the silver-specific peptide as well as a synthetic peptide based on the phage-displayed peptide sequence are able to catalyze the formation of silver nanoparticles. 40-80nm in diameter of silver nitrate (AgNO3). Here we present results on the selection of silver-specific peptides with characterization of the bio-catalyzed silver nanoparticles. We are currently investigating methods of patterning catalytic peptides as a novel approach to material synthesis.

References:

Q6.17 Oligo(phenylethynylene)5 with Reactive Side

Oligo(phenylethynylene)5 with Reactive Side
The solgel technique for the preparation of oxide materials has received significant attention because of its flexible processing parameters, and the high purity and homogeneity of resultant materials. We recently reported a non-aqueous solgel preparation of a high surface area silicon dioxide gel by the acid catalyzed ammonolysis of trimethylsilylane [Me₃Si]²⁺SiH₂⁻⁻ (TDSA). In this work we report a preparation of a high surface area silicon oximine gel via a new non-aqueous solgel process based on formamide as the gelating agent for TDSA, and the pyrolytic condensation of the gel to silicon oximine. The reaction between N,N-dimethylformamide and TDSA and formamide in a 1:2 molar ratio at 50°C for 12 h gave a transparent compact gel. After washing with ethanol followed by drying under reduced pressure, a transparent rigid aerogel was obtained. The ²⁹Si CP-MAS NMR spectrum of the gel showed three resonances at -51.8, -65.4 and -81.7 ppm with two small shoulders at -41.9 and -103.7 ppm, indicating the formation of silicon oxide and Si₃N₄ species. The ¹³C CP-MAS NMR analysis showed the presence of C₅N₁ groups (-157.7 ppm) and N-C₁ groups (38.1 and -32.2 ppm). A broad band at 933-1185 cm⁻¹ assigned to Si-O and Si-N and a strong band at 1601 cm⁻¹ assigned to C=O showed in the IR spectrum, consistent with the NMR results. The low intensity of the presence of a well-defined peak attributed to the existence of a spatial correlation of silicon oxide domains embedded in the polymer matrix. The silicon oxide particle radius and the interparticle distance are 7 ± 1 and 40 ± 2 Å, respectively. For the doped-nanocomposites the icosahedral coordination shell diminishes with the increase of oxygen concentration. For compositions up to 50% in mass ions interact with the carbonyl-type oxygen of the area cross-links at the polymer/inorganic interface. Above 10% all the amine functionalities have participated in the polymer ether-oxygen is favoured [1]. Magnetic susceptibility was measured in zero-field-cooling and field-cooling procedures. Eu³⁺-doped samples (J=0) show thermal irreversibility effects up to 150K [2]. Nd³⁺-doped hybrids show larger magnetic interactions with Nd metal and thermal irreversibility (in relative scale). This suggests that the irreversibility is not due to direct magnetic moment interactions but probably to structural effects. In fact, the Eu³⁺ magnetic moment is due to excited states (J>0), influenced by crystal field. Fe²⁺-doped hybrids show thermal magnetic irreversibility below 40K and the high temperature behaviour and paramagnetic with antiferromagnetic interactions. The Nd temperatures increase with Fe²⁺ concentration up to 16K for the highest concentration. On the other hand, Fe²⁺-doped samples do not present thermal irreversibility and the high temperature behaviour is that of a simple paramagnet.

incorporation of europium (III) β-diketonate complexes in the interlayer spacing of α-zirconium phosphate via pendant amido groups (Shane Tiemann), Anne-Christine Bravou, Daniel Zahnke, Rachel Michaux, Université Blaise Pascal and ENS-CF, Laboratoire des Matériaux Inorganiques, UMR-CNRS 6052, Aubière, FRANCE.

A lot of work has been devoted for some years to the introduction, within stable inorganic matrices, of rare-earth organic complexes which exhibit strong emissions in the visible or in the near infrared range and potentially useful for various optical applications. Almost all of these systems contain these rare-earth organic compounds related to 3D amorphous networks such as silicas or transition metal oxides whereas very few has yet been reported on bidimensional layered structures incorporating rare-earth complexes. Such systems have however a considerable interest since they can presumably take advantage of the confinement of light in the interlayer spacing and are for example expected to give rise to more important fluorescence yields. This work will focus on the irreversible insertion of rare-earth β-diketonate complexes in zirconium phosphate (α-ZrP) layered lattices which, due to their interlayer distance of ca 7.5 Å in addition to their thermal and chemical stabilities, make them suitable host matrices for bulky organic or organometallic species. The basic exchange mechanism used here for insertion involves reactions between pendant phosphonic acid groups and amino-derived difluormethylene molecules. Different routes of intercalation, including direct and indirect exchange methods or the introduction mode of the rare-earth ions, are compared. In particular, we study the influence of the synthetic pathway and of the basic strength of the amine functions on the intercalation efficiency and on the final structural and luminescent properties. The insertion of the rare-earth ions can be reached, the interlayer spacing value or the geometrical arrangement of the organic derivatives within the layered structure as the techniques that are used to characterize the final intercalated materials as well as the synthetic procedures. The metal ions are characterized by 31P and 11B NMR spectroscopies. The cationic local surroundings are also investigated by Time Resolved Spectroscopy using Eu³⁺ as an optical probe.

SYNTHESIS AND CHARACTERISATION OF TRIOTHORACEDAL ORGANO-PHYLisaLICATES. Mauoy Jakob, Bénédicte Leheux, Jocelyne Breidé, Rosan De Dree, Melanie Reau and Joséph Dentzer. Laboratoire de Matériaux Minéraux, UMR 7016, École Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace, Mulhouse, FRANCE. Institut de Chimie des Surfaces et Interfaces-CNRS, Mulhouse, FRANCE.

Hybrid materials like organophyllosilicates exhibit new properties which make them potential candidates for many industrial applications as rubber reinforcement, environmental barrier, optical application. With this aim, a series of new layered inorganic-organic solids, with organic functionalities directly bonded to the inorganic sheets via the Si-C bond, were prepared by a template sol-gel synthesis under hydrothermal conditions (room temperature) using organotrihydroxylalane as the silica source, aluminum acetylacetonate as the aluminum source, magnesium nitrate and sodium hydroxide. These hybrid materials belong to the 2:1 thoracal phyllosilicates family with interlayer distance close to 7 Å. The ratio of the metal ions could be varied between 0 and 0.33. The X-Ray diffraction patterns are in agreement with layered thoracal structure (presence of the (001) peak series and the (000) peak). The high density spacing (2.4-2.6 Å) related to the cationic species present in the interlayer space. DRIFT and 13C NMR spectra indicate that the Si-C bonds are intact and siloxanes are fully hydrolysed giving SiOAl and SiO2Mg bonds. 27Al and 29Si NMR were carried out in order to determine the different chemical state of the aluminium. Al substitutes for Si in the tetrahedral layer and Mg in the octahedral one. These results were completed by elementary analysis. The DTA-TG results show that the organic matter start to decompose in air above 250°C but its complete removal needs temperatures higher than 600°C. The aspect of the materials depends on the value of x; it varies from grey, white, waxy powder and finally powdery. The hydrophilicity of the solids being strongly depending on the aluminum content. The study of the different properties (elementary sheets or aggregates) is under progress.

RATIONAL SYNTHESIS OF MESOPOROUS ALUMINUM PHOSPHATES. Michael Tiemann1,2 and Michael Fleischer1,3. Institute of Inorganic and Applied Chemistry, University of Hamburg, GERMANY. 1Recent address: Department of Physical Chemistry, Ångström Academy, Uppsala, FINLAND. 2Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University Gießen, GERMANY.

Mesoporous aluminum phosphates with a variety of structural properties have been synthesized by use of supramolecular structure-directors. A variety of synthetic procedures have been applied, including the choice of various kinds of amphiphilic (cationic, neutral, or anionic), aqueous or non-aqueous solvents, acidic or basic pH conditions, and other parameters. Usually separate sources of Al and P have been used as reactants, e.g. aluminum oxides or phosphoric acid. In general, the exact stoichiometric composition of the obtained products has turned out to be difficult to control. Alternatively the amounts of Al and P usually differ more or less significantly from the ideal 1:1 ratio. This may be attributed to an incomplete condensation of the APO₄ network and/or for the formation of undesired by-products, such as aluminum oxide species. We report on the synthesis of mesoporous aluminum phosphates from a single molecular precursor with a pre-defined APO₄ stoichiometry and short-range structure. All products exhibit a strict 1:1 molar ratio of AlP, which indicates that the molecular unit serves as a building block in the synthesis. The materials exhibit tubular mesopores with specific BET surface areas above 400 m²/g. Further characterization includes powder XRD, 27Al and 31P solid state NMR, and IR spectroscopy.

A GENERAL SYNTHESIS ROUTE FOR MATRIX ASSISTED SELF-ASSEMBLY OF METAL-oxide CLUSTERS IN ORGANOSILICA SOL-GELS. Mokel S., Ray and Baskal C. Dave, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL.

This presentation will focus on the synthesis and use of a new organically modified silica sol-gel matrix containing ligating groups that assist the formation of metal-oxide clusters. The metal-oxide interactions can be tuned by change in external environment such that under overall neutral the metal ions are coordinated, and upon ligand desorption the metal ions to promote the growth of 4.7 nm size met-oxide clusters within the porous structure of the matrix, a) a change in pH releases the metal ions from the bound metal-oxide clusters, thereby making the sol-gel matrix behave as ferritin-apore-like analogues. Evidence of the metal-oxide interactions will be shown using UV-Vis, FTIR, TEM, AES and EDX data.

TITANIA HOMOGENEOUSLY DISTRIBUTED WITHIN THE SILICA WALLS OF MESOSTRUCTURED FILMS. Beatriz Lasnny, Guido Kickelbick, Nicola Hesing, Vienna University of Technology, Inorganic Chemistry, Vienna, AUSTRIA.

In the domain of metal oxide materials, silica-titania mixed systems have attracted increasing interest due to their considerable potential as advanced materials, catalysts and gas sensors. In general there are three methods for their preparation: precipitation, impregnation and sol-gel processing of molecular precursors. Compared to the others, the sol-gel method presents greater advantages because it allows a better control of the hydrolysis and condensation reactions. However, an important problem associated with the sol-gel synthesis is the unequal hydrolysis rate of the metal oxide precursors. For example, titanium tetrachloropropoxide is well known to hydrolyze faster than silicon oxide. For a good control over the morphology of the resulting materials, it is necessary to slow down the hydrolysis of this transition metal oxide alkoxide. In this work, a new precursor based on the ligand-assisted templating approach was synthesized by reaction of titanium oxide with a PEO based surfactant molecule [Brerett 56 or Brerett 92]. The formed coordination compound was used as a structure-directing agent in a sol containing a silica source, ethanol, water and hydrochloric acid with varied ratios of Si/Ti/Br complex. Films and powders have been prepared in a dip coating or casting procedure using evaporation-induced self-assembly. Heat treatment
resulted in the removal of the surfactant retarding the porous structure. The silica-titanium material was characterized by X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis, and transmission electron microscopy (TEM). Additionally, the catalytic activity of the titanium-silica solgel was investigated.

Q6.20 MATRIX-ASSISTED FORMATION OF METAL NANOPEARLICLES IN ORGANOSILICA SOL-GELS. Sande H. Cheung and Bakul C. Dwee, Dept. of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL.

This presentation will focus on the use of organosilica sol-gels for the in-situ formation of metal nanoparticles under ambient conditions. A specially designed organically-modified silica sol-gel precursor containing ligating functional groups has been used for regulated sequestering and binding of metal ions, and subsequent growth of metal nanoparticles within the porous silica framework. Evidence of the metal nanoparticle formation will be demonstrated with UV-Vis, FTIR, HR-TEM and EDX data. Finally, the role of the matrix in the assembly of metal sites in the pores of the organosilica solgel will be discussed.

Q6.30 VISCOELASTIC AND MECHANICAL PROPERTIES OF POLYAMIDE-CLOAY NANOCOMPOSITES. Mohamed O. Abdalla, Sharee Small and Derrick Dean Tuskes Center for Advanced Materials [T-CAM], Tuskegee University, Tuskegee, AL.

Polyamide-clay hybrids were prepared by blending in a solution of PMMA-855 in methanol. Two different clay loadings (from 5 wt. %) of PGV (an unmodified Na⁺-montmorillonite) and three organically modified-MMT (OMMT) Two of the OMMT (denoted PGV; NiCOOH, PGV; NiNH2) were prepared by surface treatment of PGV with ammonium chloride salt of a primary amine (dodecylamine) and an amino polymer (1,11-diminoundecanol-acid). The third OMMT (Cloisite-30B) was obtained commercially. The B-1 shaped nanocomposites powders were consolidated at 270°C and post cured at 316°C for 5 hours. Dynamic mechanical analysis (DMA) results showed a significant increase in the storage modulus (E') and tan delta (δ) at 2.5 wt. % clay loading nanocomposites in comparison with the neat polymer. Increasing the clay loading to 5 wt. % decreased the tan delta (δ) and E' of the nanocomposites (except the Cloisite-30B nanocomposite). The glass transition temperatures of 2.5 wt. % nanocomposites were higher than the neat polymer. A decrease in the thermal expansion coefficient was observed only for the PGV/PMD-15 nanocomposite. Tensile properties measurements for all 2.5 wt. % nanocomposites showed an improvement in the tensile modulus, tensile strength and elongation in comparison with the neat polymer. This trend in the tensile properties was not observed for the 5 wt. % nanocomposites. TGA showed slight improvement in the decomposition temperatures of the PGV:0.3HCOOH and Cloisite-30B/PMD-15 nanocomposites (2.5 wt. %) in comparison with the neat polymer. While the PVG and PVG:0.3HCOOH nanocomposites showed poorer thermal stability than the neat PMD-15.

Q6.31 FREEWAY TRANSFER BETWEEN EUROPUM AND RHODAMINE 700 IN MESOSTRUCTURED SOL-GEL THIN FILMS. Payman Minoofar, Jeffrey I. Zink, University of California, Los Angeles, Department of Chemistry and Biochemistry, Los Angeles, CA.

Numerous means of preparing mesostructured metal oxide materials by the sol-gel method have been developed over the past decade. One emerging focus in the field of sol-gel research is the "activation" of the materials with dopants that can perform "functions" such as luminescence, charge transport, catalysis, etc. In this work two luminescent components were simultaneously incorporated into a hexagonally structured silicate thin film prepared by a one-pot synthesis. The europium complex was chemically bound toward the silicate region of the film and rhodamine 700 as porphyrin primarily in the organic region of the films. These components have spectral properties adequate for energy transfer that is confirmed by excitation spectra.

Q6.32 MULTILENGTH-SCALE ORDERING OF ZnS NANOCRYSTALS USING GENETICALLY ENGINEERED BACTERIOPHAGE LIQUID CRYSTAL SYSTEMS. Seung-Woo Lee, Chunhui Mao, Christine E. Flynn and Angela M. Belcher, The University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX.

A liquid crystal system was used for the fabrication of a highly ordered multilength scale composite material using genetically engineered M13 bacteriophage and ZnS nanocrystals. The bacteriophage, which formed the basis of the self-organizing system, were selected to possess a specific recognition moiety for ZnS crystal surfaces. The bacteriophage scaffolding system was covalently coupled with ZnS solution precursors and spontaneously evolved a self-supporting hybrid film material that was ordered at the nanoscale and at the micron scale into 72 µm domains continuous over several centimeters. In addition, suspensions were prepared in which the hydrophilic liquid crystalline phase behaviors of the hybrid material were controlled by solvent concentration and by the use of a magnetic field. We anticipate that nano and multi-length scale alignment of nanocrystals using recognition moieties as well as a liquid crystalline self-organizing system can organize organic/inorganic hybrid materials.

Q6.33 METALLIC NANOPEARLICLES FROM SINGLE POLYELECTROLYTE MOLECULES. Ann Gorodyansk, Anton Kiriy, Sergey Misko, Marfred Stamm, Institut fuer Polymerforschung Dresden, Dept. Physical Chemistry and Physics of Polymers, Dresden, GERMANY.

The adsorption behavior of polyelectrolytes at a charged silicon surface is well known. At low concentrations single molecules may adsorb well separated from each other at the surface. These molecules can be used via a reaction with a metal complex in solution to generate metallic nanoparticles at the location of those adsorbed molecules. The nanoparticles have a typical dimension of 20 nm in length and four nm in width. They reveal the structure of the adsorbed polyelectrolyte molecules and their size thus also depends on molecular characteristics of the polyelectrolyte molecules. They may be used for further applications and can be removed from the surface.

Q6.34 MICROENCAPSULATION OF OIL IN ORGANICALLY MODIFIED SILICATE GLASS BY SOL-GEL PROCESS. Sung Il Seok, Bok Yeop Ahn, Joe Hyeun Kim and The Soo Suh, Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejon, KOREA

Microencapsulation is an important technique for encapsulating oil droplets within a capsule. The most widely used application of these microcapsules is the controlled release of encapsulated active agent. The functional performance and defined permeability of the microcapsule depend on the morphology, size, and the pore structures of shell. In this study, organically modified silica (ORMOSL) glasses are used as wall materials for immediately, gradually or non-releasing of the encapsulated oil. Organically modified silica glasses were prepared by the hydrolysis and co-condensation of appropriate inorganic and organic precursors such as TEOS[(ethoxypropylsilicate) and TMOS (methyltrimethoxysilane), and followed by solgel reaction. The local chemical structure of ORMOST was characterized by FT-IR, 29Si-NMR. The pore distribution and surface morphology of shell encapsulating was investigated with nitrogen sorption measurement and scanning electron microscopy. Finally, the permeability of the capsule wall was evaluated by the release rate of fragrant oil under specific environmental conditions.

Q6.35 SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS TITANIUM BY NON-PHOSPHATE SURFACTANT TEMPATING. Yuchen Shen, Guang-Qing Jiang, Ming-Jie Teng, Chun-Quan Ma, Jing-Ming Jiang, Shin-Hang Yu, Yu-Hai Liu, Jin-Yi Hong, Ling-Mei Tian Union Chemical Laboratories, ITRI, Hsinchu, TAIWAN ROC.

Since the discovery of mesoporous silicate materials by Mobil group, mesostructured metal oxides have drawn a lot of attentions from research communities. Various applications of the novel materials, such as catalyst and remediation of wastewater, were proposed and demonstrated. In addition to mesoporous silica, a variety of non-silica materials were also developed recently. Mesoporous titania is usually prepared at our laboratories using anion surfactant as a template. The surfactant template can be removed by solvent extraction or calcination techniques to form a high surface area mesoporous Titan (> 600 m²/g). The correlation between synthesis conditions and the mesoporous oxide properties was investigated. The interaction between titanium dioxide and the surfactant was characterized by NMR. The as synthesized mesoporous Titan was evaluated by means of XRD, BET and TGA and the results are reported in this article.

Q6.36 LUMINESCENCE PROPERTIES OF RARE EARTH IONS IN ORGANIC-INORGANIC HYBRID MESOSTRUCTURED THIN FILMS. Anne-Christine Ferreol, Université Blaise Pascal and ENSCCF, Laboratoire des Matériaux Inorganiques UMR-CNRS 6002, Avignon-FRANCE, Bruce Dunn, UCLA, Dept. of M&M, Los Angeles, CA; Jeffrey Zink, UCLA, Dept. of Chemistry and Biochemistry, Los Angeles, CA.
Incorporation in ordered mesostructured silica-based materials of organic functionalities has recently attracted much attention because the use of such systems in the field of optics is only emerging. Compared to amorphous silica gels, some additional benefits of the ordered pore structure for the introduction of optically active molecules may presumably be: 1. the possibility to reach higher dopant concentrations, 2. the confinement of light which can minimize the scattering losses, 3. some orientational effects. However, in view of creating new properties or enhancing the existing ones, synthetic routes that allow to deliberately choose the loading, the location and the orientational aspects for the organic species with addition to reliable methods to control the above characteristics, are still under investigation. In this study, a one-pot synthesis is used to produce hybrid mesostructured materials activated by luminescent lanthanide complexes. The materials are prepared from two different organic precursors which are directly introduced in the TEOS sol, one silylated and the non-silylated, leading respectively to a coordinated attachment of the lanthanide to the silica framework and to a simple encapsulation. Thin films are obtained by an evaporation-induced self-assembly process under acidic conditions, using CTAB as a structure directing agent. XRD patterns are always consistent with a 2D-hexagonal mesostructure, the optimal concentration of surfactant and the maximum loading of organic moieties which permits to retain a long-range order are also determined. The insertion of the lanthanide complexes in the films is clearly demonstrated by different methods and their typical strong fluorescence is observed in all cases. With europium, emission studies under selective excitation and FLN measurements can be used to probe the location of the luminescent species. Finally, the effect of the mesoporous ordering is investigated by comparing the optical properties of the hexagonally arranged materials to those of amorphous films.


Introduction: We have recently discovered a way to functionalize octaphenylsilsequioxane. Thus, we have found it possible to prepare [([ArSiO]n)]5,8(2), cubane, where Ar = Ph, BzPh, AcylPhenyl, NHCPhenyl, etc. These functionalized cubanes are 1.241.4 nm in diameter and offer rigid scaffolds for nanoconstruction projects. We discuss here octaaminophenyl cube and its derivatives, and their utility in developing new, high temperature materials.

References:

Q6.38 REGULATION OF ELECTRONIC COUPLING AND OPTICAL PROPERTIES OF METAL NANOPARTICLES J. Zheng, M.S. Stevenson, P.G. Van Heuven, Ohio University, Dept of Chemistry and Biochemistry, Athens, OH.

Dendrimer-encapsulated metal and semiconductor nanoparticles have been the subject of intense interest for optoelectronic materials and devices. We are investigating these entities as candidates for use in both electroluminescent and metalorganic (color-changing) devices. Performance characteristics in these devices are sensitive dependent upon electronic coupling between individual nanoparticles. The dendrimers associated with these particles not only act to stabilize and protect the particles, but can also provide a useful handle with the possibility to manipulate and regulate the co-association in solution and in thin solid films. We have used the well-known extinction properties of Ag and Cu nanoparticles as a probe to study aggregation and agglomeration in aqueous solutions containing these nanocomposite materials. Absorption measurements have been combined with TEM and dynamic light scattering to learn how pH, ionic strength, and temperature can be used to control aggregation of dendrimer-encapsulated Ag nanoparticles. A key objective is to understand how the aggregation state in solution translates into optical properties of solution-deposited films. The implications of this study are not restricted to Ag or metal nanocrystals; they are relevant for our understanding of the behavior of luminescent semiconductor nanoparticles as well.


Introduction: Functionalized octaphenylsilsequioxanes ([Cl3SiO]3,5,8, cubes), offer high thermal stabilities and a rigid inorganic cage structure. They offer potential building blocks for nanocomposite materials. We report here the synthesis of derivatives of octaphenylsilsequioxane, incorporating functional groups including acyl, bromo and sulfonyl chloride derivatives. These compounds provide access to novel nanocomposites, as well as to materials with photonic properties.

References:

Q6.40 NANOJET E SCALE ORGANIC/INORGANIC MULTICOMPOSITES IN SOLUTION IN THIN SOLID FILMS D.D. Richardson, S.R. Ely, M.J. Mares, M.T. Van Patten, Ohio University, Dept of Chemistry and Biochemistry, Athens, OH.

We have used functionalized poly(arylamidone) (PAMAM) dendrimers simultaneously to enclose CdSe quantum dots and to chelate luminescent lanthanide cations. The resultant structures have been characterized both in solution and in thin solid films. This new nanocomposite facilitates rapid energy transfer from the quantum dots to the luminescent lanthanide ions. This allows us to very easily combine favorable excitation characteristics of the QDs with beneficial luminescence properties of the rare-earth ions. Because each nanoparticle is closely coupled to multiple receptor ions, the QDs can produce emitting states faster than the emission decay rate. The transfer also enhances quantum efficiency by circumventing non-radiative energy losses in the quantum dot systems and allows intelligent control over emission wavelengths through selection of the rare-earth ions. Static and time-resolved photoluminescence measurements on these ensembles in aqueous solution have provided insight into their photophysical behavior. Photo, cathode- and, in some cases, electrical measurements on thin films constructed from these new nanocomposites will be presented and discussed in relation to the photophysical properties of these systems.

Q6.41 FERROSELECTIVITY OF HYBRID ORGANIC-INORGANIC POLYMIDE COMPOSITES J.J. Crosswell, Catalysis and Chemical Technologies Sandia National Laboratories Albuquerque, NM.

The permeability of a series of polyimide composites were evaluated utilizing He, H2, CO2, O2, N2, CH4, H2O, and CO2/He. Potential applications for these materials include membranes for direct methanol and hydrogen fuel cells, industrial separations, and gas separation membranes. These hybrid organic-inorganic polyimide composites were synthesized with a fluorinated block polyimide containing various concentrations of sulfonic acid groups, and an organically bridged silsesquioxane coupling-agent. Changes in morphology were evaluated with TEM, SEM, and AFM, which was attributed to the degree of compatibility between the organic and inorganic domains. The concentration of sulfonic acid groups and choice of silsesquioxane coupling-agent modulated this degree of compatibility, which governs the degree of synergetic properties exhibited by these materials. Physical property changes were reflected in changes in mean, glass transition temperature, thermal stability, and permeability changes.

Q6.42 EFFECT OF pH ON GELATION OF POLYSILSESQUIOXANES D. Schneider, Colleen Haugher, Douglas A. Low, Catalysts and Chemicals Technology Department, Sandia National Laboratories, Albuquerque, NM.

The effect of pH on the gelation time of silsesquioxanes was determined by the sol-gel polymerizations of bis(triallyloxysilyl)alkanes. While similar studies have been performed with tetraalkoxysilanes, silsesquioxanes have not been examined because few organosiloxanes form gels. Those that do gel at concentrations needed for accurate pH measurements. We were able to circumvent this problem by using bridged polysiloxanes that are known to readily form gels at concentrations low enough to allow accurate pH determination.

Q6.43 THE STRUCTURAL DEFORMATION AND MECHANICAL PROPERTIES OF PERIODIC MESOPOROUS SILICA AND
Self-assembled supramolecular arrays can act as templates for the sol-gel synthesis of organics to produce a variety of complex, 3-D nanostructured composites as mesoporous silica/surfactant composites \[1,2\].

The organic template can be removed chemically to produce mesoporous silica with 4 nm channel spacing. Polymerizing fibers within the channels can produce an inorganic/organic nanocomposite \[3\], with mechanical properties that might mimic natural composites such as nacre. In addition, periodic mesoporous organosilicas (PMO) materials have been developed recently to include a wide range of bridging organic groups (such as methylene, ethene, benzene) of the form OH-(R-Si=O)-(R-OH) \[4\]. It is not clear from the reported results whether the organic groups increase or decrease the stiffness and strength of the network. The results of experimental characterization of the mechanical properties of mesoporous silica and organosilica films and multilayers have been presented. Noncondensation has been used to characterize elastic properties and hardness at a local scale. At a macroscopic scale, film/substrate deformation experiments have been used to plastically deform the silica/surfactant composites in various stages of polymerization. The structural deformation due to applied stresses will be demonstrated using XRD, SEM, TEM and AFM. Important questions to be addressed include: how does deformation of mesoporous structures occur, to what extent elastically, and how does it compare to continuum-based models for cellular solids \[5\]?

The effect of material parameters such as structural phase (ie hexagonal, lamellar), presence of surfactant, degree of polymerization, and channel size will be addressed. Several PMO materials will be compared to silica to demonstrate the effect of incorporating bridging organic groups between silicate units on elastic stiffness.

SYNTHESIS AND CHARACTERIZATION OF POSS BASED OILS AS LUBRICANTS. Justin T. Lehnert, E.I. du Pont de Nemours & Co., Wilmington, DE, USA. Applications of POSS (Polyhedral Oligomeric Silsesquioxanes) are being studied as lubricants for solid state electronic devices.

High temperature lubricants can be useful for many applications including high performance automobile engines and jet turbines. In the highest performance systems, the lubricating fluid must be pourable at very low temperatures and be stable at higher temperatures. To this end, we have synthesized new hybrid organic-inorganic lubricants based on alkyl chains attached to silsesquioxane-based backbone systems. For example, a class of POSS based lubricants was made by the hydrolysis of long chain alpha-olefins with POSS hydrides proceeds with virtually quantitative yield. The synthesis and characterization of these materials, as well as their thermal and viscosity data will be discussed.

ORGANIC/INORGANIC NANOCOMPOSITES FROM CUBIC SILSESQUIXANES. Hijin Choi, Byung Yong Kim, Albert F. Yee and Richard M. Lane, Departments of MSE, Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI, Institute of Materials Research & Engineering, Singapore.

Octasilsesquioxan (HSiO\(_n\)\(_{18}\)) cubes have been studied extensively as nanobuilding blocks for constructing organic/inorganic hybrid composites with novel properties. Various functional groups including R = H, epoxy, methacryloyl, vinyl, Phenylacetylenyl, and ethereal have been successfully attached to these cubes and new hybrid composites have been prepared from them. Selected nanocomposites show excellent thermal/mechanical properties. Other composites offer well-defined nanostructured architecture and potentiality for applications ranging from electrodes to packaging materials to precursors for MEMS gas chromatographic analysis. We present here our latest effort to expand the library of the functionalized cubes and to develop hybrid nanocomposites.

SYNTHESIS AND CHARACTERIZATION OF NOVEL HIGH MOLECULAR WEIGHT SILSESQUIXANES. Kamyar Rahimi, Douglas A. Lea, David R. Wheeler, Sandia National Laboratories, Albuquerque, NM.

Trioxanes containing monomers of the type (RO\(_2\))\(_3\)Si(=C=O)\(_2\)OH (R = Me, Et) were prepared by hydrolysis of the corresponding vinyl tert-butyil esters CH\(_2\)CH\(_2\)C(O)OBu. Acid or base-catalyzed polymerization of the monomers leads to very high molecular weight polymers with relatively narrow polydispersities. The polymerization results in complete condensation of the alkyl groups while the tert-butyil ester functionality remains fully intact.

Partial or full deprotection of the tert-butyil group can easily be achieved to yield the corresponding polyacrylic acid polymers. The ester and carboxylic acid functionalities of these new materials allow for their potential use in a variety of applications such as ion exchange media.

A multitask microfluidic laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

CHARACTERIZATION OF TiO\(_4\)O\(_2\)(CH\(_2\))\(_6\)OCH\(_2\)\(_2\) by ELECTROSPRAY TIME OF FLIGHT MASS SPECTROMETRY. Gregory A. Khitrov, Geoffrey F. Strouse, University of California Santa Barbara, Department of Chemistry, Santa Barbara, CA.

A titanium oxide molecular cluster prepared by hydrolysis of titanium tetrachloride in the presence of methacrylic acid was characterized by electrospray - time of flight mass spectrometry (ESI-TOF).

The cluster has an approximately 38-7 nm titanium oxide core. Clusters of this type are important in potential industrial applications, and the study of silicon-inorganic hybrid materials as well as intermediates in the sol-gel preparation of glass and ceramic materials. The primary result of this study is a fingerprint mass spectrum of the title compound.

Fingerprint spectra reveal useful information about the organization of more complex chemical systems such as reaction mixtures of glass, ceramic, or hybrid material precursors. The chemistry of such systems is not well known and ESI-TOF is a powerful technique for studying the reactions of clusters in solution. While ESI-TOF has been applied to the study of titanium oxide hydrolysis processes, mass spectra of isolated individual titanium oxide clusters have not previously been reported.

OPTICAL PROPERTIES OF CdSe NANOSECOND DOPED SOL-GELED. Daniel Neuman, Peter Ford, Geoffrey Strouse, University of California at Santa Barbara, Dept of Chemistry and Biochemistry, Santa Barbara, CA.

In the present study, CdSe nanocrystal are being embedded in silica based sol-gels using &aminopropylmethoxysilane (APS) as a precursor. Semiconductor nanomaterials have well known size dependent optical properties and high surface to volume ratios. This gives rise to optical properties that can be tuned by passivation and environmental effects. Introducing these materials onto solid-state supports has shown to enhance their stability towards decomposition. Moreover, sol-gels provide a porous structure [pores on the order of 30 nm in our material] that can allow the diffusion of small molecules to the imbedded nanocrystals. Small molecules, such as dioxygen and water have been shown to activate photoluminescence in these materials. Time resolved emission is being used to investigate the excited state decay kinetics of the imbedded nanocrystals, and the influence of surface sensitivity to small molecules including nitric oxide.

SYNTHESIS AND CHARACTERIZATION OF HOLLOW SPHERES INCORPORATED WITH MAGNETIC NANOPARTICLES. S.M. Safir Rahman, Xiaowei Teng, Hong Yang, University of Rochester, Department of Chemical Engineering, Rochester, NY.

Organic-inorganic hybrid nanocomposites with a focus on tailored functionality and morphology has attracted much attention in recent years. Assembly of polyelectrolytes on micron-sized polystyrene spheres becomes an important subject because of various applications of spheres-based technologies. Layer-by-layer assembly is a straightforward method that can be readily adopted for making functional structures. Our primary interest focuses on the magnetically sensitive systems. We will report our work on the synthesis of hollow polymer/magnetic nanocomposites incorporated with magnetic nanoparticles such as ferrite (Fe\(_3\)O\(_4\)) and FePt sandwiched in polyelectrolyte. We have also synthesized magnetic nanoparticles-lipase composites. The structures of hybrid magnetic hollow spheres made by layer-by-layer assembly and those made by lipase encapsulation have been examined using DSC, AFM, SNOM and TEM. The stability of these hollow spheres under the magnetic field has been analyzed using optical microscope and fluorescence confocal microscope.
A combination of solution and solid phase chemistry has been used to synthesize new nonoxide-based surfactant/inorganic composites with nanoscale periodicity. These composite materials in a perovskite framework templated by cetyltriethylammonium bromide surfactants. Small and high angle x-ray scattering along with elemental analysis are used to characterize the structure and composition of tin-telluride based composite materials. The nanoscale order is a result of a multi-step synthesis and processing scheme. Potassium titn telluride clusters, synthesized in the solid state, co-assemble with the quaternary ammonium surfactants in formamide solution. Oligomerization of the telluride clusters appear to favor chloride density making between the ionic surfactant micelles and the inorganic species which results in the precipitation of a layered semicrystalline composite. Mild thermal treatment of the as-synthesized composite in the solid state results in further oligomerization of the inorganic framework, accompanied by the liberation of bulk tellurium. The recognition of the inorganic framework also results in evolution of the nanoscale periodicity from the layered phase to a periodic two-dimensional hexagonal architecture. The tellurium can be selectively removed by using tributylphosphate to yield the final composite material. These results demonstrate that the concept of solution phase inorganic/organic co-assembly can be extended from sol-gel type oxides to nonoxide materials.

Q6.52 STUDY HYBRIDS ORGANIC AND INOR OGANIC PMMA
PMMA/HEMA CONTAINING DYES Tran Kim Anh, Phan Thi Minh Chau, Nguyen Trung Quan, Tran Tho Ha, Nguyen Vu Le Quoc Minh, Inst of Mtls Sci, Natl Ctr for Natural Sci and Tech of Vietnam, Hanoi Do, Cau Giay, Hanoi, VIETNAM.

Our work focuses on solid matrices PMMA/PMMA/HEMA to dope the organic dyes. The hybrid matrix obtained by the sol-gel method from two components (TEOS) in which blended different polymers. The dyes are Rhodamin 6G(Rh6G), Coumarin 540 (C 540) which were embedded in these matrices. The properties of these dyes in the different matrix were investigated by using the measurements such as Human mesothelial cell hydration, fluorescence, photoluminescence excitation spectra and lifetime.

Q6.53 FLUORESCENCE AS A MOLECULAR PROBE OF MISCELLANEOUS IN ORGANIC/INORGANIC HYBRID NANOCOMPOSITES FOR MICROELECTRONIC APPLICATIONS Q.R. Huang, Carlos W. Frank, Dept. of Chemical Engineering, Stanford, CA David McReeeyes, James L. Hedrick, Willy Vilsen, Robert D. Miller, IBM Almaden Research Center, San Jose, CA.

Fluorescence spectroscopy has been used to study the miscibility of MS/Q/PMMA-co-DMAEMA) hybrid nanocomposites, which are useful in fabricating the new generation of spin-on ultralow dielectric constant materials in the microelectronic industries. In this work, we have attached two polymer groups into the PMMA side chain with different amount of initial -SOH (silanol) endgroups are used to study the effect of endgroup functionality on the phase separation behavior of the hybrid nanocomposites. Pyrene excimer fluorescence results reveal that MS/Q is miscible with P( MMA-co-DMAEMA) only up to 6 wt.% P(MMA-co-DMAEMA) loading level. As the P(MMA-co-DMAEMA) loading level increases, the excimer to monomer ratio also increase, suggesting that the MS/Q/MMA-co-DMAEMA) hybrid nanocomposites move toward greater immiscibility. The fluorescence results also show that, the lower the amount of initial silanol groups in MS/Q, the greater the immiscibility of the hybrid nanocomposites. In contrast, differential scanning calorimetry (DSC) results indicate miscibility for P(MMA-co-DMAEMA) loading levels as high as 70 wt.% for both MS/Qs studied.

Q6.54 GAS ADSORPTION STUDIES OF AMINO-FUNCTIONAL INORGANIC-ORGANIC HYBRID MATERIALS Noriko Yamada, Takao Kusama, Yuji Kubo, Keiyo Kawakami and Takashi Hamada, Advanced Technology Research Laboratory, Nippon Steel Corporation, Chiba, JAPAN.

Inorganic-organic hybrid materials offer advantages for adsorbent, separator, sensor, etc. because of their versatility of the combination of both inorganic and organic components and the ability to tailor porosity. One of the most important requirements to realize such applications is high selectivity, which may be attained by the control of chemical affinity. In the present study, the affinity-control of inorganic-organic hybrid materials has been attempted by the introduction of various amino groups. Amino-functional inorganic-organic hybrid powders containing amine groups (AP), diaminomethylimine groups (DAMIM) and diethylenamine groups (DEAP) were prepared from optically pure alkylsilsesquioxane with each amino groups and tetraethoxysilane (TEOS) in a molar ratio of 0.25:0.75. Amino-functional hybrid powders were exposed to NO, NO2, and SO2 at a 0.5% mixture in argon for 24 hours. The effects of the amino groups with AP, DAMIM and DEAP-functional hybrid materials were followed using a thermogravimetric analyzer by directly exposing the hybrid powders to 0.5% acidic gases. Because the amino-functional hybrid powders are thought to adsorb water vapor and other gases when exposed to ambient air, amino-functional hybrid powders were thermally regenerated in dry argon gas prior to all sorption studies. Negligibly small increase of weight was observed for the amino-functional hybrid powders exposed to NO. The adsorption amount of NO2 was larger than that of SO2 in all the amino-functional hybrid powders. The selectivity (the adsorption amount of NO2 / that of SO2) and the sorption capacity were found to be affected by the kind of amino groups. DAMIM-functional hybrid showed the largest sorption capacity to both NO2 and SO2.

Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

Q6.55 HYBRID ORGANIC-INORGANIC MATERIALS DESIGNED FOR CLEAN WASH IN PHOTOGRAPHY DIGITAL PHOTOGRAPHY GENESIS OF A SOL-GE INDUSTRIAL PRODUCT: THE KODAK WATER SAVING TREATMENT SYSTEM Jean Guillement, Didier Martin, Olivier Poncelet, Kodak Industrie Research Lab, Chaton Sur Sarthe, FRANCE.

Environmental laws concerning the water become more and more stringent year after year in European Union (AT25/91 in France, Legge Metti in Italy). The classical silver halide photoprocessing requires at least 3 steps which are the development, the fixing and the washing. The water usage step uses a huge amount of water which is discarded in the sew. In July 2000 in a French Law imposed that the volume of wash water has to be divided by 5 and the nature of pollutants (silver) has to be maintained below 1 mg/l. The Kodak Water Saving Treatment System has been designed to help our customers to be in compliance with the Law. This system has 2 functions, the release of biocides cocktails and the trapping of silver. Two similar elements (immobilized-like material) allow the treatment to occur, the first one release biocides in the water flow and allow the processor to remain clean, the second one is an hybrid organic-inorganic composite (immodified by controlled hydrolysis of two organic siloxane alkoxides) allows to trap silver. These 3 elements are extremely robust versus time and chemical (pH). This paper will describe the synthetic way, their characteristic (Hartner) and the obtained performances in various configurations after one year on the market. Other applications of these hybrid organic-inorganic composites in photographic fields will be also discussed.

Q6.56 UNIQUE GLASS TRANSITION BEHAVIOR OF THE Ni-P ALLOY COATED POLYMER MICROSPHERES. Zhengqi Shao, Liang Hong, National University, Dept of Chemical & Environmental Engineering, SINGAPORE

A thin Ni-P alloy has been successfully coated onto polymer microspheres with an average diameter of about 50 micrometer. Two types of polymer microspheres used are poly(methyl methacrylate) and poly(acylamidomethane) networks respectively. We have observed that the glass transition ranges of the polymer materials shift apparently towards lower temperature direction when they are enclosed by the metallic alloy shell. This interesting thermal response could be identified only when the average particle size of polymer microspheres is smaller than 100 micrometer, which suggests that the metallic coating can facilitate quick establishment of a uniform temperature field within the polymer because that has a diameter below 100 micrometer. In addition to using Ni-P alloy, this study has also examined other metallic coatings, such as copper and silver. An identical polymer matrix displays inconsistent glass transition behaviors with the change of the metal clothe. It is anticipated that these physical properties of a polymer matrix in connection with the movements of segments will be altered in a more profound way with the rise of the interfacial area between the metallic coating and the polymer substrate.

Q6.57 HYBRID ORGANIC-INORGANIC REVERSE OSMOSIS MEMBRANE FOR BACTERIAL ANTIPOLLUTING Sung Hee Kim, Sung Yeop Park, Seoul National Univ, School of Materials Science and Engineering, Seoul, KOREA.

Hybrid organic/inorganic reverse osmosis [RO] membranes composed of the aromatic polyamide thin films undergo that the titanium dioxide
Organic-Inorganic Phases have a central role in "Organised matter chemistry", a quickly developing area that holds its place at the crossroads of materials chemistry, physics and biology. The construction of these networks can be tailored by the use of external templates such as the hydrolysis-condensation of the metallic cations with the self-assembly of the organic counterparts. While much progress has been attained in silicon-based materials, interest and positive results in transition metal (TM) oxides-based systems are increasing. The control of the higher reactivity of TM relative to Si (i.e., retarding the condensation process) is essential for a successful synthesis. Evaporation-Induced Self Assembly (EISA) is an interesting alternative to prepare TM oxide-based mesostructures. In this work, mesostructured TiO2-surfactant hybrid xerogels and thin films, presenting hexagonal mesostructure (p6mm) are obtained from ethanol/H2O media, after selective solvent evaporation. The formation kinetics of the mesostructure is followed by XRD, interfacialometry and MS. The role of the parameters affecting synthesis and processing conditions (concentration of reagents, environment, temperature, nature of the hybrid interface) is discussed together with their influence on the obtained mesostructures. Organised Titanium oxides are reproducibly formed through cooperative self-assembly between hydrophilic Ti-Oxono mesosilica building blocks and the micellar template. The hydrophilic matching approach proposed in this work has been extended to other titanium systems, using low or non-surfactants. For non ionic surfactants, strongly acidic conditions allow the blurring of specific template/inorganic bonding, and the essential interactions are focused on the compatibility of the hydrophilic character at the hybrid interface. Thermal treatment of these titanias based hybrids leads to high surface (350-400 m2g⁻¹) phosphorous-free mesoporous titania, the mesostructure is retained at a temperature as high as 350°C. This approach can be successfully extended to other nonphillic-based mesostructured materials.
characterize the final film. The inorganic-organic copolymer template offers the interesting possibility to convert parts of the template molecules into backbone groups that ultimately define and shape the wall of the inorganic framework by a simple heat treatment. Investigations of the thermal degradation process by solid state NMR showed that the PEO block can be selectively degraded at 250-350°C, while the PDIEN block is completely degraded at 600°C. Heat treatment at 450°C results in a hydrophobic inorganic-organic hybrid material which still shows a well ordered mesostructure and in which the PDMS chains are partly attached to the silica walls. 

10:00 AM Q7.5  
FORMATION OF HYDROGEN BONDS BY SUSPENSION POLYCONDENSATION USING HYDROPHILIC BLOCK COPOLYMERS  
Geraldine Gerdau, Nicolas Ségui, Frédéric Di Renzo, François Fajula, CNRS-Ecole Nationale Superieure de Chimie, Montpellier, FRANCE; Olivier Anthony, CNRS Rhône Complex Fluids Laboratory, Cranbury, NJ.

Double hydrophilic block polymers were used to control the growth of inorganic particles and prepare hybrid colloidal suspensions. Colloids of metal hydroxide oxides were obtained by forced hydrolysis of metal ions in presence of water-soluble diblock copolymers. The block copolymers contain one metal-complexing polyether block and one neutral solvating block that does not interact with metal ions. The role of the first block is to ensure a controlled growth of the inorganic phase in the complexing functions as inorganic condensation; the second block ensures the colloidal stabilization. Phase diagrams presenting the conditions under which precipitation is inhibited are established. The colloids are then characterized in terms of surface charges, sizes and morphologies. The main parameters controlling the size were identified: the copolymer-to-metal ratio, the metal prehydrolysis ratio and the ratio between the polymer block lengths. The synthesis route yields, first, fully solvated micelles, and then produced micelles in the hydrophilic block copolymers. It is due to complexation of the metal precursors by the polyether blocks leading to insoluble complexes. Further investigations are in progress to obtain complete structure. The second step consists in inorganic condensation, leading to mineralization of the micellar core and thus to polymer-protected particles. The suspension polycondensation process leads to highly reactive particles whose morphologies depend on the nature of the metal and on some specific synthesis parameters. Small-angle neutron scattering, light scattering and transmission electron microscopy were used to characterize the particle geometries.

10:30 AM #Q7.6  
NEW HYDRO MULTIFUNCTIONAL MESOPOROUS MATERIALS: SUBSTITUTION OF OXIDE AND ORGANIC MOIETIES OF PERIODIC MESOPOROUS ORGANOSILICA MATERIALS BY HETERATOM FUNCTIONAL GROUPS.  
Tozodara Ade, Neil Coombs, Hilfrid Groendy, Mark J. MacLachlan, Geoffrey A. Overy, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, ONTARIO, CANADA; M. jetar Jaroniec, Michel Kurz, Department of Chemistry, Kent State University, Kent, OH.

Unique properties and application opportunities of nanocomposite materials have continued to inspire much interest in the development of new multifunctional advanced inorganic-organic hybrid materials. We recently developed various synthetic routes to a new class of hybrid materials containing periodic mesoporous organosilica (PMOs) having molecularly integrated organic/inorganic networks, high surface areas, pore volumes and uniform pore sizes and that show many new chemical, physical and surface properties. Here we present, various chemical and thermal routes that successfully substitute the organic and oxide groups of these materials by heteroatomic functional groups forming new types of multifunctional nanocomposites that are otherwise impossible or difficult to prepare by other methods. These novel materials find applications in gas storage, gas separation, sensors and electronic packaging, environmental remediation and acid scavengers.

11:00 AM #Q7.7  
CONTROL OF SURFACE FUNCTIONALITY IN TEMPLATED MACROPOROUS OXIDES.  
Andreas Stein, Rick C. Schroeder, Mohammed Al-Dous, Hongwei Yin, University of Minnesota, Dept of Chemistry, Minneapolis, MN.

Colloidal crystal templating is a versatile method to synthesize porous solids with periodic, three-dimensional arrays of interconnected void spaces, typically with controllable unit cell parameters. The templated synthesis can be employed to produce porous structures with walls composed of oxides, metals, semiconductors, polymers, and hybrid structures. The periodic porous structures impart the materials with interesting optical properties, highly accessible internal surfaces, and the ability to trap and stabilize relatively large guest species. All of these properties may be optimized by modifying the surfaces with organic functional groups, either directly during the templated synthesis or following formation of the porous support by grafting processes. This talk will focus on surface functionalization of mesoporous silicates containing mesoporous walls, macroporous titania, and macroporous zirconia. The surface groups are used to control adsorption/desorption of guest molecules, ions, and catalytically active clusters. The effects of organic functionalization on the mechanical properties of the macroporous oxides and issues of access into the pores will also be discussed.

11:30 AM Q7.8  
PREPARATION OF MESOPOROUS Si-M[Al]$_{1}$ OH$_{2}$ VIA A NON-AQUEOUS SOL-GEL ROUTE.  
Fei Cheng, Berangere Toury, Ralf Suplicy, John S. Bradley, Department of Chemistry, University of Hull, UNITED KINGDOM.

The sol-gel technique has been established as an important route to new oxide materials with interesting structures and morphologies. Recently we have developed a non-oxide sol-gel method for the preparation high surface area silicon dimide Si[Al]$_{1}$OH$_{2}$ (precursors to high purity Si$_{3}$N$_{4}$ by acid catalyzed amonolysis of tris(dimethylamino)silylamine [Me$_{3}$N]$_{3}$SiNH, 1, and 2,6-di(dimethylamino)silylamine [Me$_{3}$N]$_{2}$SiNH$_{2}$, 2) were prepared from the lithium salt of [Me$_{3}$N]$_{3}$SiNH$_{2}$ and aluminium trichloride or trichlorohydroxosilane respectively A transparent semi-sol Si-Al inside gel 3, and an amorphous Si-oxide inside gel gel 4, were prepared by acid catalyzed amonolysis of 1 or 2 in dry THF. Evaporation of the solvent and the dimethylamine, produced in these reactions, in a stream of nitrogen followed by drying under reduced pressure yielded white powders. The IR-spectra of both gels showed broad ν(N-H) bands at 3200-3550 cm$^{-1}$, suggesting the presence of NH groups with different environments. Bands at 735 cm$^{-1}$ in the IR-spectrum of gel 3 and 1479 cm$^{-1}$ in the spectrum of gel 4 can be ascribed to Al-N and B-N bonds respectively. Both gels showed ν(Si-N) and ν(N-C) at 1180 and 920 cm$^{-1}$ respectively. The low intensity of ν(CH) bands from 2796 to 2933 cm$^{-1}$ for both gels indicated the presence of detectable amount of residual dimethyl amidine groups. These spectral bands identify the gels as silicon and aluminum boron oxides, containing residual dimethylamino groups: Si[Al]$_{1}$OH$_{2}$, [Si$_{3}$N$_{4}$], [Me$_{3}$N$_{2}$SiN$_{2}$], [Me$_{3}$N]$_{3}$SiNH, [Al$_{2}$O$_{3}$]. TG-MS analysis of the gels showed that dimethylamine and ammonia were evolved below 200°C, consistent with the IR results. Both gel exhibited mesoporous structures and had total surface areas of 928 m$^{2}$/g for 3 and 692 m$^{2}$/g for gel 4.


11:45 AM #Q7.9  
Abstract withdrawn.

SESSION Q8: TEMPLATED GROWTH TO NANO/MESO/MACRO-STRUCTURED HYBRIDS  
Wednesday Afternoon, April 3, 2002  
Metropolitan I (Argent)

1:30 PM #Q8.1  
BLOCK COPOLYMER-DERIVED ORGANIC HYBRID MATERIALS FROM ORGANICALLY MODIFIED CERAMIC PRECURSORS.  
Uli Wiesner, Cornell Univ, Dept of MSE, Ithaca, NY.

The study of amphiphilic block copolymer based functional polymer-inorganic hybrid materials is an exciting emerging research area offering enormous scientific and technological promise. By choice of the appropriate functional groups as well as the correct precursors unprecedented morphology control on the nanoscale is obtained. It is based on a unique polymer-ceramic interface. The hydrophilic parts of the polymer are completely integrated into the ceramic phase analogous to what is found in biological hybrid materials. The structures generated on the nanoscale are a result of a fine balance of competing interactions, another feature of complex biological systems. This potential for new functional materials lies in the versatility of the polymer chemistry as well as that of the silicate chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructured materials will be presented with potential applications ranging from microelectronics to medicine. Examples will include the preparation of mesoporous materials with pore sizes ranging from 5-50 nm for separation technology and catalysis as well as the synthesis and characterization of novel model block copolymer nanocomposites.
ORDERED INORGANIC ORGANIC COMPOSITES AND POROUS SOLIDS. Brad Chmelka, University of California, Dept of Chemical Engineering, Santa Barbara, CA.

Substantial recent progress has occurred in the development of ordered inorganic-organic composites and porous inorganic materials with versatile properties for a variety of applications. Such materials can be prepared using structure-directing block copolymer or low-molecular mass surfactant species that allow control to be exercised over material compositions, ordering, dimensions, and architectures that span length scales ranging from less than a nanometer to centimeters. The organic species provide processability and structure-directing functions, while the inorganic components yield robust frameworks. The physiochemical processes involved are generally complicated, because of the heterogeneous, multicomponent, and non-equilibrium natures of these systems. In particular, interactions between hydrophilic, hydrophobic, inorganic-organic, and air-liquid interfaces are crucial to the development of molecular, mesoscopic, and/or macroscopic orientational order in these materials. Recent results and perspectives will be presented on the underlying self-assembly mechanisms, processabilities, and structures of ordered inorganic-organic composites and porous solids. Such materials show promise for an increasingly diverse range of applications in opto- and microelectronics, catalysis, separations, structural solids, etc., several of which will be highlighted.

PERIODIC MESOPOROUS ORGANOSILICAS WITH DIFFERENT ORGANIC BRIDGING LIGANDS - SYNTHESIS AND CHARACTERIZATION. Vivien Rebin, Michael Froba, Justus Liebig Univ, Inst of Inorganic and Analytical Chemistry, Giessen, GERMANY; Olaf Muth, Univ of Hamburg, Inst of Inorganic and Applied Chemistry, Hamburg, GERMANY.

In 1999, a new way was found to incorporate organic moieties into M1S silica materials [1]. For the first time bridged silsesquioxane precursors, e.g. 1,2,5(1,2,5)triazacyclohexane, were used as linker source in the synthesis of highly ordered hybrid mesoporous materials (PMOs) in order to integrate bridging organic groups directly into the framework of the pore wall instead of grafting these organic species onto the pore wall surface. In this study we present results on the synthesis of PMOs with different aliphatic and aromatic organic bridging ligands synthesized under alteration of the reaction parameters. Different structure directing agents lead to a variety of well defined pore diameters with narrow pore size distributions. PMOs with pore diameters in the range of 3 to 13 nm could be realized [2]. Nitrogen physisorption revealed high specific surface areas of more than 1,000 m²/g. The well ordered structures were characterized by XRD, TEM and SAXS measurements. Spectroscopic methods confirmed the preservation of the organic spacers after the hydrothermal synthesis and subsequent extraction of the surfactant molecules.

SYNTHESIS AND CHARACTERIZATION OF MESOSCOPICALLY ORDERED SURFACANT/CO-SURFACANT TEMPLATED METAL OXIDES. Mikhail C. Mohn, Tamas Csernyavesi, Jessica Rosenholm, Dept. Phys. Chem. Abo Akademi University, Abo, FINLAND; Freddy Kleitz, MPI-Kohlenforschung, Mülheim a.d. Ruhr, GERMANY.

This communication concerns an approach to enhance the swelling of both siliceous and non-siliceous composite mesophases through the addition of surfactant-organic swelling agents with or without the use of nonionic cosurfactants under acidic conditions. This approach has proved very useful in the synthesis of large pore silicas under basic conditions. The d-spacing of hexagonally ordered titania and zirconia composite mesophases could be increased up to 80 Å (TEM/CTAB molar ratio = 4) without the loss of the long-range order of the hexagonal mesophase. Increasing the TEM content further lead to a transition to a lamellar phase through a hexagonal-lamellar coexistence regime. TEM was much more efficient than close in swelling the mesophase, which is opposite to what has been observed under basic and room temperature conditions. The swelling of the hexagonal mesophase of titania could further be increased through the use of cosurfactants, the octanol/TEM molar ratio being the key parameter in preventing a hexagonal-to-lamellar phase transition. For zirconia, the addition of 1-octanol generally led to the formation of a hexagonal-lamellar or lamellar mesophase. In contrast, losses of ordered structure both in titania and zirconia was usually observed upon removal of the template. On the contrary, the d-spacing of SBA-3 type 2D hexagonally ordered silica could controlably be increased by the same approach, closely indicating the potential of the use of mixed surfactant systems together with a swelling agent for the synthesis of large pore mesoporous materials.

SESSION 8: ADVANCED PROCESSING FOR HYBRID MATERIALS

Chair: Kenneth J. Balkus and Christopher J.A. Barbe
Thursday Morning, April 10, 2012
Metropolitan II (Argent)

8:00 AM *Q8.1 MICROSTRUCTURAL EVOLUTION WITH TEMPERATURE OF 300
MESOPOROUS SILICA FILMS STUDIED BY FTIR SPECTROSCOPY: Filippo Innocenti, Paolo Falcaro, Dipartimento di Ingegneria Meccanica, Sensores Materiali, Università di Padova, Padova, ITALY; David Grosso, Chimie de la Matière Condensée, Université Paris 6, Paris, FRANCE.

Silica mesoporous thin films have been synthesized with a self-assembly process employing cetyltrimethylammonium bromide as the organic template and tetramethyl orthosilicate as the silica source. Mesoporous films with 3D-Hexagonal and 3D-Cubic phases have been obtained with different protocols of synthesis. The materials are of interest for a variety of applications including catalysis, separation, and drug delivery. The evolution of the micromorphology has been studied with transmission Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of the as-deposited films have shown the presence of cyclic aggregates, revealed by two absorption bands at about 1150 and 600 cm⁻¹, whose intensity gradually decreased with the thermal treatment. At temperatures larger than 350°C cycled-silica have been more observed. In the 1000-1300 cm⁻¹ region several overlapped absorption bands have been detected. In particular, we have detected the pair LOR-TO₄, the cyclic species absorption band and the pair LOR-TO₃. These last bands, in particular are associated with order-disorder transitions that is the microstructural evolution that we observe for temperatures around 300°C when the cyclic species are broken and a larger local disorder in the silica pore walls is introduced. The evolution of the bands in the 1000-1300 cm⁻¹ region has been better understood with the Berreman configuration, perming the FTIR analysis at 45° with respect to the normal incidence angle. The LOR band, which in silica-sol-gel films is indicative of the network condensation and is activated by scattering of the light in the pores, was resolved as a single sharp band from 250°C. As temperature increases, the LOR to TO₄ pair is almost completely disappeared, in accordance to order-disorder transition of the silica microstructure. The TO₃ band has been used to evaluate the residual porosity in the films at the different heating stages, we have obtained values in good accordance to what reported in literature for measures with other techniques.

8:30 AM #Q9.2 DAM1: MOLECULAR SIEVE FORMS, FILMS AND FILMS. Kenneth J. Balkus, Jr., Deok Coutinho, Suhail Nadirgul, Claudia Meek, Paul Paratone, University of Texas at Dallas, Department of Chemistry and the UTD NanoTech Institute, Richardson, TX.

The evolution of new molecular sieves and associated applications has generated a greater demand for new ways to manipulate and configure nanomaterials. The required form of a molecular sieve may involve dramatically different length scales, ranging from shape particles to colloidal, solution, and filmic forms. Efforts in this area will be illustrated using various examples of these forms based on Dallas Amorphous Materials one (DAM1). This mesoporous molecular sieve was synthesized using the EPTGS as the template molecule. In addition to potential drug delivery applications for this inorganic/organic composite, the hierarchical forms DAM1 may be employed in areas ranging from catalysts to sensors. The morphogeny of DAM1-1 applications in molecular recognition and optical sensing will be described. We have also developed a novel process for spinning DAM1 molecular sieve fibers that will be presented. Additionally, our patented method for the fabrication of zeolite membranes, using pulsed laser deposition (PLD) will be discussed. As part of this effort a new technique for line patterning DAM1 films was developed.

9:00 AM #Q9.3 MICROSCOPIC REPLICAS VIA THE CHEMICAL VAPOUR DEPOSITION OF CERAMICS. Gary Cook, Christine G. Spickermann, Peter L. Timms, University of Bristol, UNITED KINGDOM.

A novel method has been devised to coat nanometer- and micron-size structures with ceramic oxides via chemical vapor deposition (CVD) at low pressures and room temperature. The oxides form on the surface of the substrate (template) by reacting silane and siloxane/hydride mixtures with hydrogen peroxide vapour. This CVD method has several advantages over current sol-gel techniques. It does not dissolve the template or alter its structure, it uses less reactants, it allows a range of compositions to be formed, it is independent of the substrates surface properties (e.g. hydrophobicity) and it yields exact replicas. The method has been applied on a variety of electroplated polymer fibres and has now been extended to the replication of three-dimensional biological structures such as butterfly and fly wings. Potential applications of the hybrid structures as well as the purely inorganic replicas are discussed.

9:15 AM #Q9.4 PATTERNING OF ORGANO SILICA SOL-GEL SURFACES. Balaji C. Joneja, Milk I. S. Raghavachari, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL.

Sol-gelled silica sols exhibit gradual yet reproducible variations in the physical state along the sol-gel transition structure. Thus, starting from a molecular precursor, one can obtain a liquid sol which has the ability to condense into a solid transparent glass. As such these materials provide unique opportunities for patterning by selective deposition, using phase imprinting techniques. Hence, the geometrical features of the template can be easily imprinted onto the viscous sol prior to gelation. Once the gelation takes place, the physical imprint of the template becomes permanent on the surface of the final material. This presentation will discuss the use of our lab for inducing geometrical order into organosilica materials by means of using suitable templates. Finally, some of the novel application of these materials as microdevices will be elaborated.

9:30 AM #Q9.5 INFLUENCE OF ORGANIC MODIFIERS ON THE ADHESION OF HYBRID COATINGS. C.J. Burke, B.A. Linne, M.I. Ignat, D. Cosslett, K. Finnie, J. Haman and J.R. Burton, ANSTO, Menai, AUSTRALIA.

Organic-inorganic hybrids obtained by sol-gel processing offer a versatile new approach for fabricating thin films for a wide range of applications, including sensors, waveguides, integrated optics, and corrosion and scratch resistant coatings. A critical issue for industrial applications of these coatings is their fracture behaviour and adhesion to substrates. By controlling process variables such as the nature and volume fraction of the organic group and the heat treatment temperature, the mechanical properties of the hybrid coatings can be readily adapted for specific functions. To investigate the influence of both the connectivity of the inorganic network and the nature of the organic modifier on the final mechanical properties, a series of thin coatings were deposited on polycarbonate and stainless steel substrates by spin-coating mixtures of TEOS and selected alkylmethoxy silanes (MTMS, VTMS and GPTMS). The influence of the organic modifier during processing was monitored by FTIR spectroscopy and the connectivity of the inorganic network in the corresponding bulk gels was assessed by 29Si MAS NMR studies. Simulacron, an in situ microscopic testing and optical microscopy was used to probe the fracture and adhesion behaviour of the coatings. The mechanical properties of the coatings were found to be strongly modulated by the size of the organic modifier. In particular, increasing the size of the organic substituent led to a corresponding increase in the ductility of the film, together with improved adhesion. The relationship between the connectivity of the inorganic network, the volume fraction and size of the organic modifier, and the mechanical response will be discussed.

9:45 AM #Q9.6 MICRO- AND MESPOROSITY OF TRIBLOCK COPOLYMER-Templated SILICA. Characterisation and CONTROL. Francesco Di Renzo, Anne Galaheme, Hekene Cambon and Francois Fujita, INSTM, Catalytic Material Laboratory, Montpellier, FRANCE.

Silica triblock copolymer mesoporous zeolites are effective precursors for ordered mesoporous oxides [1]. SBA-15, a hexagonal mesopore formed in the presence of EO38PO78EO38 surfactant, differs from MCM-41, a mesoporous mesostructured silica material with the same textural properties. This difference is due to the microporous presence in the silica wall between the main channels [2]. The geometry of the mesostructure affects the adsorptive properties and the application of the usual methods of pore size evaluation. It is shown in which way the pore structure of SBA-15 varies with the synthesis conditions. The microporosity, arising by structuring of silica and interface comb structures of poly(ethylene oxide), can be controlled by modifying the interactions between surfactant and solvent. The effects observed represent a general pathway to control the density of the inorganic moieties in composite mesostructures and the secondary voids inside the inorganic moiety. 1. D.Y. Zhao, Q.S. Hao, J.L. Feng, B.F. Chelmke & G.S. Stucky, J. Am. Chem. Soc., 1998, 120, 39-43. 2. M. Impéron-Clerc, P. Davidson and A. Davidson, J. Am. Chem. Soc., 2000, 122, 11955. 3. P.I. RaviKovich and A.V. Neiman, J. Phys. Chem. B, 2001, 105, 6884. 4. A. Galaheme, H. Cambon, F. Di Renzo and F. Fujita, Langmuir, in press.

10:30 AM #Q9.7 PHASE SEPARATION IN ALKYL-BRIDGED POLYSILSES.


Phase separation and concurrent sol-gel transition behavior of polymerizing bis(3-trimethoxysilyl)alkanes has been investigated under acidic conditions. Concurrent spinodal decomposition and sol-gel transition of hydroxylated bis(3-trimethoxysilyl)alkane are the resultant two well-defined co-continuous phase-separated structures. The phase separation tendency was found to be much lower than those in alkaline solutions and quite low in the neutral range. After release, sharply distributed macroplates were obtained in the size range of 0.1 to 5 μm and twigs-like thin-continuous gel domains were observed.

10:45 AM Q9.8

EXPLORING THE ROLE OF NANOSCALE SCALE ARCHITECTURE ON HIGH-PRESSURE DEFORMATION IN PERIODIC SILICA/SURFACTANT COMPOSITES.
Sarah H. Tolliver
We, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA

In this presentation we explore the unique structural properties of periodic silica/surfactant lamellae and ordered mesoporous silicas. Our results indicate that under hydrostatic compression, these composites can be as stiff as bulk silica, but that deformations are more elastic. At modest pressures (up to ~4 GPa), small angle X-ray scattering is used to determine the volume compressibility. In the composites, this compressibility is found to be essentially identical to that of bulk vitreous silica despite the high organic fraction (> 60 volume %). Moreover, nanometer scale architecture can produce materials that are stiffer than the predictions of continuum theories. At higher pressures, deformations of the nanometer scale periodicity are observed, but unlike the pressure-induced distortions seen in bulk silica, these remain reversible under decompression. Luminescence from probe molecules located within the pores indicates that the silica framework supports the applied load and that a more fluid environment exists within the pores, even at very high pressures. These results are unified by the results of high-pressure infrared spectroscopy. Modeling the peak shifts shows that at modest pressure, the local silica bonding distances in much the same way that bulk silica distorts under pressure. At higher pressures (above 4 GPa), atomic scale distortions cease and are replaced by distortions on the nanometer length scale. These nanometer scale distortions are more reversible than the atomic scale distortions that occur in bulk silica, thus explaining the unique combination of high stiffness at moderate pressures and good elasticity at high pressures.

11:00 AM Q9.9


A new approach for depositing polymer/inorganic hybrid films using gas phase deposition technology has been developed and is the focus of this work. These films combine the high hardness and scratch resistance of inorganic hybrid films with the flexibility and toughness usually associated with softer polymeric films. The gas phase deposition process eliminates several of the key problems associated with the traditional wet chemical preparation of hybrid materials, including contamination in the precursor synthesis and the elimination of harmful solvents from the process. In addition, gas phase deposition processes generate inherently denser materials than wet chemical processes eliminating post deposition annealing procedures that may damage the substrate. In this study, films are deposited on polycarbonate (PC) and silicon substrates using a novel plasma reactor. In this system, a TEOS/O2 gas stream is injected into a high density plasma (1 kW maximum power) generating inorganic SiO2 active species which are incorporated into a growing plasma polymer film. Films are grown from the precursor TEOS, TMSi and TPS with high and low pressure conditions. Characterization of the hybrid materials is performed by spectroscopic ellipsometry. The dependence of the film properties is assessed for changes in the precursor concentration and the deposition conditions.

We have developed a novel synthesis route to a variety of semi-conducting and metallic mesoporous films through a combination of electrochemistry and surfactant templating methods using a dilute surfactant solution (~5 wt%). An electric field applied during the deposition process can provide a very unique and extreme environment for charged-electrolyte interface. This unique environment can be exploited to electrodeposited mesoporous films possessing high surfactant molecules to the plating solution that will form charged surfactant-inorganic aggregates. When the electric field is applied, these aggregates are driven to the electrode and form thin liquid-like crystalline phases. As a result, the mesoporous structures will be fabricated into the deposited films. This new method provides an easy, fast, inexpensive, and versatile route to the production of various metal/metal oxide films with thermally stable mesoporous framework. In this presentation, we will discuss the detailed synthesis conditions, which can provide the most effective cooperative interactions of inorganic species, structure-directing agents, and the electric field. The effect of synthesis parameters on the film morphologies and mesoporous structure will be presented. The resulting films exhibit significantly improved electrochemical performance towards methanol oxidation, indicating that the high surface areas are electrochemically active and demonstrating the technological importance of these films.

11:30 AM Q9.11

OPTIMIZATION OF RADICAL PHOTOPOLYMERIZATION IN HYBRID SOL-GLASS GLASSES: ADVANTAGE OF BICOMPONENT PHOTOACTIVE SYSTEMS. Olivier Soppa, Ciments Craoix-Baugur, Christian Carre, Dept. of Photochemistry, CNRS UMR 7525, Mulhouse, FRANCE.

Use of organosilanes as hybrid systems is of increasing importance for their promising applications in the optical field. Considerable attention was already paid to the study of the inorganic network. However, poor information concerning the organic part involved in the sol-gel process is available. This is yet a fundamental requirement for optical applications where homogeneity at molecular scale is essential. Taking into account the specificity of the sol-gel medium, the chemical and photophysical properties of the organic part have to be adapted to the optimization of the properties of the final material. Hybrid materials used in this study consisted of organosilane precursors with methacrylate functions, titanium isopropoxide, methacrylate acid and photoinitiator. The polycrystallization of the inorganic component was achieved sequentially and simultaneously with the photopolymerization of the organic ones to provide a mutually interpenetrating network. Photopolymerization in the UV range presents the advantages of fast-curing at temperatures compatible with fragile substrates and spin-cast-temperature selectivity of the reaction. Characterization of the photopolymerization process taking place in hybrid sol-glass materials were investigated by UV and Real Time FTIR spectroscopy. Besides the study of the organic network, NMR investigations led information relevant on the inorganic network formation during the photopolymerization. The whole results provide insights into the optimization of the photocrosslinked step. Indeed, it was demonstrated that titanium components added as passive components to increase the refractive index of polymeric layers can induce polymeric layers. Moreover, the acid component provided mechanical strength due to its high refractive index. The addition of polymerization inhibitors. The UV process can be improved by using an organic photoinitiator and titanium components were investigated and led to a better efficiency of the photoinitiator. Final materials with higher conversion ratio of the methacrylate function and requiring shorter irradiation time were achieved.

SESSION Q10 ADVANCED PROCESSING FOR HYBRID MATERIALS AND CHARACTERIZATION METHODS

Chair: Kuniki Nakumura and Jean-Francois Gerard

1:30 PM Q10.1

TOWARDS HIGH RESOLUTION III-V SOLID STATE NMRI SPECTRA IN HYBRID MATERIALS. L. Cusma, V. Goletto, C. Bonhomme, F. Balzani, Chimie de la Matiere Condensee, UPMC, Paris, FRANCE.

A large class of hybrid materials for applications in the fields of protective coatings, optical devices, sensors, catalysis prepared by trapping organic, or even biological entities within a sol-gel matrix. The spatial distribution of the organic entities within the inorganic network depends on the specific interactions that can be developed between the guest molecule and the host. The optimization of the material properties is a good understanding of this interactions. 1H MAS-NMR can be a nice tool to characterize the
organic entities, that can be either trapped, or covalently grafted to sol-gel network. But, under standard experimental conditions, the spectra offer no clue to the nature of the 1H-1H dipolar coupling that usually exists in these highly protonated systems. Commercial MASNMR probes are now available that can reach spinning rates up to 35 kHz, and thus allow to record high 1H-NMR spectra, especially when combined with high magnetic field (11.7 T). The utilization of such technique will be illustrated on two types of hybrid systems: silica matrices doped with various dyes and mesostructured hybrid silicates templated by surfactant post-synthesis approaches. In both cases, emphasis will be put on the characterization of the spatial proximity between the host matrix and the molecule.

2:00 PM Q10.2
TEMPLATING IN NONPOROUS SILSEQUIOXANES: SOLID-STATE NMR STUDIES. Peter A. Mirza and Shu Yang, Lucent Technologies, Bell Laboratories, Murray Hill, NJ.

High-resolution proton and silicon solid-state NMR has been used to study structure formation in solution mixtures and composites of ethylene oxide/propane oxide triblock copolymers and methyl silsequioxane. These mixtures are precursors to porous ultra low dielectric constant films used in the fabrication of integrated circuits. The solution NMR results show that micelle formation is suppressed during solvent casting and curing of the films, and that the miscibility is maintained until late in the curing process as a result of the interactions between both the ethylene oxide and propylene oxide blocks of the triblock copolymer with the methyl silsequioxane matrix. The results show that the domain size and the interdomain structure depend on the polymer architecture. The fully cured films show low dielectric constants, low moisture uptake and good electrical and mechanical stability, and are suitable for the next generation of integrated circuits.

2:30 PM Q10.3
LIGHT-DRIVEN IN-SITU SYNTHESIS OF Ag NANO PARTICLES AND NANOWIRES TEMPLATED WITHIN SELF-ASSEMBLED SILICA MESOPOROUS THIN FILMS. Yi Yang, Univ. of New Mexico, Center for Micro-Engineered Materials and Advanced Materials Lab, Albuquerque, NM; Weiling Gong, Werner Lutze, Catholic Univ. of America, Vitreous State Laboratory, Washington, DC; C. Jeffrey Brinker, UNM, Center for Micro-Engineered Materials and Dept. of Chemical and Nuclear Engineering, Sandia National Laboratories, Albuquerque, NM; John A. Shelnutt, Sandia National Laboratories, Univ. of New Mexico, Dept. of Chemistry, Albuquerque, NM.

Tin protoporphyrin, a photocatalytically active metalloporphyrin complex, is an effective photosensitizer for reductive growth of heavy metals. The assembly of mesostructured silicon thin films offers a potential means for incorporating such photocatalytically active agents into mesopores. Tin protoporphyrin-containing mesoporous silica films can then be used to adsorb silver ions (along with a weak electron donor) from an aqueous solution. Then, upon irradiation, the silver ions are reduced to elemental silver through the photocatalysis of tin protoporphyrin fixed in the mesoporous thin films. In the constrained environment of the pores, the properties of Ag nanoparticles were controlled by the concentration of the tin protoporphyrin and the porosity of the silica. In particular, the size of metal particles and the width of the nanowires were controlled by the size and structure of the silica. TEM imaging showed that Ag nanoparticles in the pores have diameters of 1 to 3 nm with narrow size distribution depending on the size of mesopores templated by different surfactants. The success of this process offers a range of applications, from cleaning up heavy metal contaminated water to photolytic degradation of metal nanowires.

2:45 PM Q10.4
SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF MIXED-PHASE MICROPOROUS-MESOPOROUS MATERIALS. Raju H.P.R. Polad, Christopher Landry, Univ of Vermont, Cook Physical Science Bldg, Burlington, VT.

Mixe-phase microporous-mesoporous materials have been produced by a two-step synthetic process. These solids, called MM1, [MM1-1(MFI) phases] and MM2-2 (MCM-48/MFI phases), have been characterized by X-ray diffraction (XRD), nitrogen adsorption and electron microscopy. At early stages of crystallization at 170°C, mesoporous phases were formed exclusively, while at later heating times MFI was formed. At intermediate times, MM1-1 were formed with varying amounts of MFI depending on the crystallization time. XRD indicated that MM1-1 could be severely oriented by simple prebaking, which was consistent with an unusual ribbon-like morphology observed in TEM. This morphology was not observed for either pure MCM-41 or MFI. All-MM1-1 was also synthesized, and was used for the isomerization of xylene. These experiments showed that Al-MM1-1 has a higher selectivity for m-xylene than either Al-MCM-41 or Al-MFI [25-5]. Finally, Ti-MM1-1 was synthesized under similar conditions to the oxidation of alkenes. IR spectroscopy indicated that the mixed-phase material contained framework Ti species and has more amorphous order within its walls than Ti-MCM-41. Ti-MM1-1 was shown to be more selective for alkene oxidation than either Ti-MCM-41 or Ti-MFI (TS-1).

3:15 PM Q10.5
CHARACTERIZING POROSITY IN NONPOROUS THIN FILMS USING POSTIRradiATION ANNihilation LIFETIME SPECTROSCOPY. David Gidley, William Frazer, Department of Physics, University of Michigan, Ann Arbor, MI; Jianing Sun, Hu Yifan, Department of MSE, University of Michigan, Ann Arbor, MI; Shu Yang, Bell laboratories Lucent Technologies, Murray Hill, NJ.

Depth profiled positronium annihilation lifetime spectroscopy (PALS) has been used to probe pore characteristics (size, distribution, and interconnectivity) in thin, porous films, including silica, organic, and hybrid films. PALS has good sensitivity to and resolution of all pores (both interconnected and closed) in the size range from 0.3 nm to 30 nm. In this technique a focused beam of several keV positrons forms positronium (Ps, the electron-positron bound state) with a depth distribution that depends on the selected positron beam energy. Ps inherently localizes in the pores where its natural (vacuum) annihilation lifetime of 124 ns is reduced by collisions with the pore surface. The collisionally reduced Ps lifetime is correlated with pore size and is the key feature in transforming Ps lifetime distribution into a pore size distribution. In hybrid films made porous by a degradable porogen PALS readily detects a percolation threshold in porosity loading that represents the transition from isolated to interconnected pores. PALS is a non-destructive depth profiling technique with the only requirement that positrons can be implanted into the porous film where Ps can form.

3:45 PM Q10.6
MASS SPECTROMETRY ANALYSIS OF ORGANIC-INORGANIC NANOMATERIALS AND THEIR PRECURSORS. Jean-Philippe Guermeur, USTMC, Metz University, Metz, FRANCE; Geoffrey Srouse, Dept. of Chemistry, University of California, Santa Barbara, CA.

Current methods for analyzing nanomaterials have centered on physical methods, such as NMR, TEM, X-ray diffraction, XPS, UV/Vis, IR, Raman and photoluminescence spectroscopies. These analytical tools are excellent for measurement analysis of a cluster or a nanomaterial, however, the specific distribution in composition and structure of individual nano-material is not addressed. Mass spectrometry methods [MS] using soft ionization processes (electrospray [ESI], laser desorption/ionization [LDI] and matrix assisted laser desorption ionization [MALDI]) are alternative pathway for providing information concerning the identity, functionality and stability of organic materials. We have successfully applied mass spectrometry to the analysis of i) nanoscale semiconductor (Cd/Zn -S), ii) materials up to 3 nm in diameter such as titantium oxide containing a TiO2 core, which can be precursor of organic polymeric network in addition to an inorganic network, combining properties of inorganic and organic materials. By ESI, soft ionization techniques were found all of the materials in the negative ion mode consistent with fragmentation along crystallographic planes. Application of mass spectrometry methods based on LDI and MALDI techniques have also been applied to provide insight into the light sensitivity and the decomposition of the clusters.

4:00 PM Q10.7
UV SENSITIVE HYBRID SOLS FOR THE MANUFACTURE OF THICK PZT FILMS. P. Ray, S. Salhot, Promic, Levallois, FRANCE; P. Paulus, A. Jacobelli, Thales Research and Technology, Orange, FRANCE.

There is a strong demand for PZT sol-gel precursors that will simplify greatly the technological process of preparation of thin or thick PZT films, more particularly in application like low cost non-volatile memory (e.g smart cards?), passive components integration (e.g mobile phone impedance adaptation filters?) or MEMS (transducers, actuator...) [3]. This can be firstly achieved by diminishing the number of deposition steps for a certain thickness to be reached. However for thick films, cracks are generated during the calcination and can be prevented only on small surface regions. So a patterning process is also necessary prior to densification. A hybrid sol-gel process includes ACAC and an HMTA/acetic acid system. This formulation allows the tuning of the viscosity in a range from 10 cSt to 3000 cSt. Full wafer layers, having a final thickness from 200 to 1000 nm, have been deposited in one deposit without cracking. Films with a total thickness of several μm have been also prepared, with few deposition layers and with dielectric or piezo-electric properties close.
to that of bulk ceramics. UV patterning of 400µm squares was made and a final 0.6µm thick PZT has been obtained with no cracks and a very good adhesion with the silicon. These conditions show a very high yield in PZT oxide. Sol with oxide contents as low as 12% can be used to prepare 250 nm film in one deposit. This represents an advantage in term of efficient treatment. Thick inorganic films with high oxide yield have been prepared with sols with high organic content and with the advantage of organic chemistry.

SESSION Q11: PROCESSING AND PROPERTIES OF FUNCTIONAL HYBRIDS (OPTICAL, ELECTRICAL, MECHANICAL)
Chair: Shu Yang, John R. Bartlett and Jean-Pierre Boilot
Friday, Morning, April 5, 2002, Metropolitan II (Argent)

8:30 AM *Q11.1
ENERGY AND ELECTRON TRANSFER BETWEEN MOLECULES IN MESOSTRUCTURED SOL-GEI THIN FILMS
Jeffrey I. Zink, Raquel Hernandez, Anne-Christine Franville, Pagram Minas, Bruce Dunn, Department of Chemistry and Biochemistry, University of California, Los Angeles, CA.

Three strategies for placing molecules in deliberately chosen regions of mesostructures synthesized by a dip-coating or dip-spinning technique are demonstrated. These strategies all involve one-step, one-pot syntheses where all of the components are present in the sol from which the substrate is pulled. Silicate films templated by surfactants contain three-dimensional networks, the organic region formed by the hydrocarbon tails of the surfactants, and the intervening ionic interface formed by charged surfactant head groups, the counterions, and residual solvents. Each of these regions has unique physical and chemical properties that are exploited in order to control the placement of molecules. The molecules chosen in this demonstration of the techniques are luminescent, and spectroscopy is used to verify the locations of the lumophores. The first and simplest method uses hydrophobic molecules that are located in the hydrophobic organic region. The spectra, solvatochromism, and fluorescence depolarization not only confirm the location but also provide information about the local dynamic properties. The second method uses planar complexes into the silicic framework via co-condensation of a silated ligand. The emission properties and the luminescence lifetimes demonstrate that the complex is part of the framework. The third method places an ionic ruthenium complex at the ionic framework interface by tethering it to the silicic framework via the silated alkyl terminus of its ethylenediamine ligand. The position of the luminescent ruthenium complex is verified by the luminescence band maximum. Pairs of molecules are placed in spatially separated regions, and dynamic processes such as energy and electron transfer are demonstrated.

9:00 AM *Q11.2
ACTIVE INHIBITED MATERIALS BY NANOSCALE CHEMISTRY AND NANOPHOTONICS
Jean-Pierre Boilot, Sophie Besson, Valerie Buissette, Frederic Chiquiti, Thierry Giroux, Arnaud Hugnard, Nathalie Landraud, Jacques Peretti, Physique de la Matiere Condensee, UMR 8545, Ecole Normale Superieure, Palais de Cedex, FRANCE; Sophie Besson, CNRS/St-Gobain, UMR 8125, Aubervilliers, FRANCE; Christian Ricoult, Laboratoire de Mineralogie Cristallographie, UMR CNRS 7590, Paris 6 et 7, Paris Cedex 05, FRANCE.

We present different arrangements of hybrid nanodots for optical applications: 1. Highly luminescent 400µm colloids II-VI quantum dots are prepared through the grafting of organic molecules at their surface. These nanocrystals can further be used as building blocks for the synthesis of well defined nanomaterials. For instance, highly luminescent transparent films for integrated optics are obtained by using VVO₄₃₅ nanocrystal-silica composites. 2. Random networks of quantum dots are prepared by gelation of colloids. As in the silic system, the transparent percolating structure can be described as homogeneous assemblies of fractal clusters whose sizes are inferior to visible-range wavelength. 3. Ordered arrays of quantum dots are prepared by a confined growth of nanocrystals in silica mesoporous films. Using these templates, the 3D ordering of nanoparticles is obtained at a large scale on different substrates. These high density arrangements of nanocrystals are required in different applications such as semiconductor lasers. 2. Dense arrays of nano-dots are optically excised by using near-field optical patterning of photostable nano-hybrid films with sub-wavelength resolution. This provides potential applications to optical lithography and high density optical data storage with a capacity of at least 1 Gb/cm². 3. 9:30 AM Q11.3
OPTICAL RESPONSE OF DENDRIMER-ENCAPSULATED CdS QUANTUM DOTS IN THIN FILMS-REGULATION OF INTER-PARTICLE ELECTRONIC COUPLING
D.D. Richardson, S.R. Elly, M.J. McMurdo, P.G. Van Patten, Ohio University, Dept of Chemistry and Biochemistry, Athens, OH.

Dendrimer-encapsulated metal and semiconductor nanoparticles have been the subject of intense interest for new optoelectronic materials and devices. We are investigating these entities as candidates for use in both electroluminescent and metachromatic (color-changing) devices. Performance characteristics in these devices are sensitively dependent on electronic coupling between individual nanoparticles. In another work, we have demonstrated the ability to regulate inter-particle electronic coupling between metal nanoparticles based on the solution-phase properties of the dendrimers used. Here, we apply the knowledge derived in these studies of metal nanoparticle systems to learn about the effects of electronic coupling on the optical response of the CdS quantum dots. Changes in solution properties (pH, ionic strength, and temperature) lead to spectral band shifts and changes in quantum efficiency. Some of these changes are predicted to better understand, predict, and optimize optical response in thin film devices containing these quantum dots.

9:45 AM Q11.4
INORGANIC-ORGANIC POLYMERS AS PHOTO-PATTERNABLE DIELECTRICS FOR MULTILAYER MICROWAVE CIRCUITS
Lothar Frechlich, Ruth Holzberg, Stephan Jacob, Michael Popall, Framoher-Institut fuer Siliciumforschung, Waerburg, GERMANY; Roland Meudt-Faeder, Jürgen Graf, Thomas Reiche, Germany, Gerlingen-Schillerhoche, GERMANY; Marco Munk, Manco Communications GmbH, Freiburg, GERMANY; Haso von Zychlinski, UniWeChemLanj, Mittelwalde, GERMANY.

Inorganic-organic hybrid polymers (ORMOCERS) combine very good optical and dielectric properties in the lower high frequency range (ε = 3 and tan δ = 0.004 at 1 MHz). This is particularly promising for electro-optical applications. However, the production of thin-film multi-layer microwave circuits for high frequency (up to 100 GHz), e.g., for radio-frequency (RF) applications requires extraordinary material properties such as a low permittivity ε < 3, a dielectric loss tan δ of about 10⁻⁵ and a higher thermal stability for temperatures up to 300°C (lead-free soldering). Main objectives of the material development was to set up a series of ORMOCER materials suitable for thickness up to 300µm stable materials, demanding voltages were 250 V/cm and thickness as thin as 150 µm and additionally be patterned by UV lithography with sufficient photo-crosslinking resolution. Therefore, the synthesis of novel ORMOCER resins starts from styrene-substituted organosilanes and siloles as precursors for photo-crosslinking in combination with organic crosslinking of polymeric organic functions. A series of UV patternable materials was developed, which have been tested at high frequencies up to 40 GHz, exhibiting dielectric properties of ε = 2.5 and tan δ = 0.001.


10:15 AM *Q11.5
FROM CONDUCTING POLYMERS TO HYBRID ELECTRO-ACTIVE MATERIALS
Pedro Gomez-Romero, Instituto de Ciencia de Materiales de Barcelona (ICMUB), Bellaterra, SPAIN.

The multifunctionality of conducting organic polymers (OPVs) has been responsible for the wide range of applications targeted for these materials. But in addition to their remarkable intrinsic properties, OPVs provide a solid base for the development of hybrid nano-composites. This conference will address the different possible approaches, materials and applications that can be developed based on conducting polymers and modified graphene nanosheets. Although materials and applications are ever growing in number, we will center our discussion on systems based on organic compounds with electrochemical or photoelectrochemical activity which could be harnessed to develop electroactive hybrid materials.

10:45 AM Q11.6
USE OF SOL-GEI HYBRIDS FOR LASER OPTICAL THIN FILMS
Philippe Belleisle, Philippe Preit, Claude Bounin, Yves Moncoutoir, CEA/Le Ripault, Monts, FRANCE.
The CEA/DAM megajoule class pulsed Nd-glass laser levers to Inner Confinement Fusion (ICT) research is required 7,000 m of coated area onto 10,000 optical components. Among these different optics, two specific examples of applied solid-glass chemistry will be described. First, one deals with the 280 4x4 cm cavity-end mirrors comprising highly reflective silicon dioxide deposited onto deformable substrates. Such mirrors are using stacks of SiO2 and ZrO2-PVP (PolyVinylPyridine) thin films, both starting from solid-coated colloidal suspensions (solv). The ZrO2-PVP high index layer is a nano- composite material prepared using non-aqueous, two-component suspension with a transparent polymer solution (PVP). The oxide/polymer ratio of the composite system has been optimized regarding refractive index value and laser damage threshold. UV-curving of the nano-composite has enabled optical coating stacking up to 20 layers, achieving 99% minimum reflection over the whole coated area. FT-IR spectroscopy has been used to identify chemical interactions and polymer modifications under UV-irradiation. The so-developed HIL-curing process has been transferred to production plant for CEA mirror supplying. Second example is concerning development of a silica-based hybrid material to protect silver-coated light reflector used in laser pumping cavity. These metallic reflectors require a protective overlayer in order to preserve high-reflectivity front surfaces for long periods of operation under intense broadband flashlamp light and typical airborne contaminants. The so-called armo-coating has been optimized in term of thickness and composition to enhance silver resistance to oxidation under UV-irradiation, to protect silver layer from cleaning procedure, to withstand 10,000 flashlamp light-impulses exposure with the lowest possible damage per flash and with lowest reflectance value. To fulfill those requirements, the hybrid material acts as an oxidation barrier, is chemical- and scratch-resistant, is durable and remain transparent in the 400-1000 nm range. Moreover, the sol-gel process allows coating deposition onto large-sized and multi-shaded reflectors. These new protected reflectors employed in current solid-state lasers will ensure both higher performance and lower operating costs.

11:15 AM Q11.7

**CONDUCTIVE POLYMER/TRANSITION METAL OXIDE HYBRID MATERIALS FOR LITHIUM BATTERIES**

Chiu-Wen Kwon, Armel Poquet, Stéphane Moret, Guy Campet, Jean-Pierre Forges, Institute of Chemistry of Environments, UMR CNRS 5270, Bordeaux Cedex, France, and A. Vidal-Miran, B.B. Kale, Center for Materials for Electronics Technology, Ministry of Information Technology, Govt. of India, Panipat, India, India.

Organic-inorganic hybrid materials were synthesized for use of lithium battery electrode by following two strategies: 1) core-shell strategy for tri-dimensional transition metal oxide and 2) intercalation strategy for 2-dimensional (lamellar) transition metal oxide. We choose conductive polymers as an organic component for their high electric conductivity and transition metal oxides as an inorganic counterpart for large capacity and processibility. Poly(pyrrole)/graphite and poly(3,4-ethyleneoxythiophene) (PEDOT)/vanadium pentoxide hybrids were prepared and compared with graphite powder for core-shell and intercalation strategies, respectively. Poly(pyrrole)/graphite showed an enhanced electrochemical reversibility and capacity up to 370 mAh/g in the potential range between 1.5 and 0.0 V vs Li at 3 A/g. PEDOT/vanadium pentoxide also exhibited improved reversibility and capacity up to 328 mAh/g at 15 mA/g between 2.0 and 4.4 V Li on the second discharge. XRD, IR, electron microscopy, XPS and X-ray absorption spectroscopy were used to characterize the samples, and to examine oxidation state of the transition materials, doped character of the polymer and the nature of interrelation between the polymer and the transition metal oxides.

11:30 AM Q11.8

**OPTICAL PROPERTIES OF CONJUGATED OLEFIN AND POLYMER DOPED MESOSTRUCTURED SILICA/BLOCK-COPOLYMER COMPOSITES**

Brian J. Scott, Michael H. Bartl, Galen D. Stucky, University of California, Santa Barbara, Dept. of Chemistry and Biochemistry, Santa Barbara, CA.

Doped mesostructured and mesoporous materials are emerging as a new class of optical and organic component for their high electric conductivity and transition metal oxides as an inorganic counterpart for large capacity and processibility. Poly(pyrrole)/graphite and poly(3,4-ethyleneoxythiophene) (PEDOT)/vanadium pentoxide hybrids were prepared and compared with graphite powder for core-shell and intercalation strategies, respectively. Poly(pyrrole)/graphite showed an enhanced electrochemical reversibility and capacity up to 370 mAh/g in the potential range between 1.5 and 0.0 V vs Li at 3 A/g. PEDOT/vanadium pentoxide also exhibited improved reversibility and capacity up to 328 mAh/g at 15 mA/g between 2.0 and 4.4 V Li on the second discharge. XRD, IR, electron microscopy, XPS and X-ray absorption spectroscopy were used to characterize the samples, and to examine oxidation state of the transition materials, doped character of the polymer and the nature of interrelation between the polymer and the transition metal oxides.

1:30 PM Q12.1

**CHEMORHEOLOGY AND MECHANICAL PROPERTIES IN RELATION TO THE MORPHOLOGIES OF HYBRID ORGANIC-INORGANIC MATERIALS: A REVIEW**

Jean-Francois Giraud, Hamid Kaddoumi, Laboratoire des Matériaux Microencapsulation (LM2E) UMR-CNRS 5027, INSA Lyon, Villeurbanne Cedex, France, Laboratoire de Chimie Organique
Macromolecules, Université Cadi Ayyad, FST-Gafgui, Dept. Chimie, Marrakech, MOROCCO.

This paper proposes a review of the literature on the relationships between morphologies and mechanical properties of organic-inorganic nanocomposites synthesized from sol-gel chemistry of metal alkoxides. In all the cases, the low strain (dynamic mechanical) and large strain (modulus, ability of plastic deformation, fracture) behaviors can be related to i/ the morphology (purity and state of condensation of the phases controlled by the conditions of the sol-gel reactions of metal alkoxides, temperature, time); ii/ the nature of the interactions in the organic-inorganic interface. The analysis of the changes during the synthesis, i.e. chemothermoelectric of the reactive system, contribute to a better knowledge of the generated morphologies.

2000 PM *Q12.2* HYBRID CATALYTIC NANOSTRUCTURES. Thomas Bein, Jörg Reder, Chris Huber, Dirk De Vos, Steven B. Ong, and Gang Xu, Department of Chemistry, University of Munich, Munich, GERMANY.

In this presentation, we will discuss different strategies for the incorporation of catalytic activity into mesoporous and mesoporous nanomaterials. Such strategies include grafting or encapsulation of selective molecular catalysts and sequential reorganization cycles of encapsulants/active species. Typical examples include metal oxide clusters and metal coordination complexes in zeolite hosts, metal alloys and metal and metal oxide clusters encapsulated in mesoporous materials, and mesoporous/inorganic chiral catalysts encapsulated in mesoporous hosts. Mass transfer in such systems can be controlled by the sorption properties and the structure of the channels. Control of morphology permits the development of thin film formats for efficient activity enhancements. Thus, catalysis and catalyst precursor complexes were covalently attached to high surface area, accessible mesoporous films of various thicknesses (up to 1000 nm) and were obtained with block-copolymer surfactants. Different attachment strategies have been explored, including post-synthesis surface reactions or co-condensation of linker molecules such as glycidoxypropyltrimethoxysilane, followed by covalent grafting of porphyrin complexes such as tetrameric (2,9,16-tris[(3aminophenyl)methyl]-porphyrin. These catalytic containing mesoporous nanomaterials exhibit activity in selective catalytic oxidation reactions, thus demonstrating the extraordinary versatility of porous hosts for the design of functional hybrid systems.

2300 PM *Q12.3* PARTICLE-LAYERED ORGANIC-INORGANIC HYBRID COATINGS AS CORROSION INHIBITING SURFACE TREATMENTS FOR ALUMINUM ALLOYS. Tommy L. Metcalfe, Olga Kachurina, Edward T. Knowles, Oklahoma State University, Environmental Institute, Stillwater, OK.

Hybrid organic-inorganic films (Ormosil) have been found to provide a good resistance to metal substrates and are a replacement for solution-cast Nature's own conversion coatings. In this study, sub- to micro-sized particles (TiO2, Al2O3, SiC, TiN) were found to significantly improve the corrosion protective properties of the Ormosil coatings as determined using electrochemical and accelerated salt spray methods. Structure-property relationships are being investigated to understand the observed corrosion resistance characteristics.

2455 PM *Q12.4* POLYMERIC-ZEOLITE NANOCOMPOSITE MEMBRANES FOR GAS SEPARATION. Huaing Wang, Limin Huang, Yushan Yan, University of California, Riverside, Department of Chemical and Environmental Engineering, Riverside, CA.

Gas separation by polymer membranes is an important area of research. The key advantages of a polymer membrane are that they are inexpensive and can be fabricated into compact modules such as hollow fiber with very high separation area/volume ratio. However, polymer membranes usually have relatively low selectivity, significantly limiting its widespread applications. Zeolites are microporous aluminosilicates with uniform pores and have been widely used in powder composite form as molecular sieving separation media. Zeolite crystals have been previously incorporated into polymer membranes to improve their selectivity. At present, however, most studies use rather large zeolite crystals (e.g., micrometers). And there is no success example of polymer-zeolite composite membranes with high selectivity so far because of the interfibrillar incompatibility and defects between zeolite crystals and polymer matrix. Successful preparation of advanced composite membrane requires solving both material selection and defect elimination problems. We have been studying a new approach to incorporate zeolite nanocrystals into polymer matrices with good dispersibility in organic solvents that is compatible with polymer matrix, helping eliminate interfacial defects of composite membranes. Zeolite nanocrystals have been successfully prepared in our laboratory. However, they usually contain organic template inside the pores. Template-free zeolite nanocrystals are obviously required for the purpose of membrane application. Thus far, the most commonly used method for template removal is through high temperature calcination. This method is not suitable for colloidial zeolite nanocrystals because it leads to severe irreversible aggregation. We have recently developed a novel technique for the preparation of re-dispersible zeolite nanocrystals in solvent (H2O), to yield a kind of re-dispersible template-free zeolite nanocrystals in promising for membrane application. In this presentation, we will show our efforts in detail on the preparation and characterization of zeolite nanocrystals (e.g. silicone and A) filled polymer (e.g. polysulfone) composite membranes. Gas permeation measurements show that composite membranes have better gas separation properties than pure polymer membrane.


3:00 PM *Q12.5* POLYSULFONE-BASED THIN FILMS WITH HIGH PHOTOSENSITIVITY. Gregory M. Jamison, Kelly Simmons-Potter, B. G. Potter, Jr., Carol C. Pflueger, Sandia National Laboratories, Albuquerque, NM.

A great deal of research has been done to understand the photo-sensitized optical response of inorganic glasses, which exhibit a permanent, photo-induced refractive index change (DN) due to the precipitation of optically active photochromic dyes. In the present work, we have investigated the intrinsic photosensitivity of a family of poly[arylmethyl]silanes and poly[diarylsilanes for use in photonic waveguide devices. Limited testing of passive optical behavior (e.g. absorption, refractive index, photosensitivity, and thermal behavior) was performed for our material in thin-film form. It was determined that the materials exhibited dramatic photo-blowing under 248 nm (KrF excimer laser). Based on a Kramers-Kronig analysis of the absorption changes, refractive index changes on the order of 0.1 are confirmed. Determination of this calculation has been provided via ellipsometry which estimates refractive index changes at 0.02 at a wavelength of 0.414±0.001. In addition, embedded strips have been phototransferred into the material to confirm waveguiding capacity of the films. Possible sources of photosensitivity in this material and its potential for application in various device configurations will be discussed.

Sandia is a multimission laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

3:15 PM *Q12.6* THE SYNTHESIS, CONDENSATION, AND LUMINESCENCE OF OLOPHENYLENEDIVINYLENE) WITH ALKOXYCHLOR SE AND GROUPS. Heiner Deter, Elke Sugiono, Johannes Gutenberg University, Mainz, Germany.

Due to their strong fluorescence, stilbene oligomers are one of the preferred classes of luminescent materials for electrophotographic applications. The good solubility of alkoxysubstituted OPVs is advantageous for the processing of these materials, but limits the fabrication of multilayer devices. Additionally, the stability of amorphous films from these semiconductors is poor. This paper presents the synthesis of numerous oligophenylenedivinylene with curable units, either terminal vinyl groups for thermal crosslinking or alkoxysilane moieties for curing via silicon bridge. The alkoxysilanes are rigidly connected to the chromophores via Heck reactions or cross-metathesis with vinylalkoxysilanes. Hydrolysis and subsequent condensation yields oligosiloxanes with pendant OPVs, thus greatly improving the film forming capability of these materials well defined chromophores. The connection to cyclosiloxanes and oligosiloxanes has a distinct influence on the electronic spectra of the OPVs in the solid films. Additionally, conjugated systems with high electron affinity like 2,5-diaryl-1,3,4-oxadiazoles are functionalized with alkoxysilane oligomers. These materials are interesting for the preparation of organic-inorganic hybrid materials with luminescent building blocks.

3:30 PM *Q12.7* CONDUCTING AND MAGNETIC HYBRID ORGANIC INORGANIC MOLECULAR. Lahmène Ouahab, Stéphane Golhen, F. Iwahori, Université de Reims I, France, Akira Miyazaki, Toshihiko Enoki, T.I.T., Tokyo, Japan, Jun-ichi Yamada, H.I.T., Himeji, Japan.

This paper presents the synthesis of organodiphenyl alkoxysiloxane oligomers with curable units, either terminal vinyl groups for thermal crosslinking or alkoxysilane moieties for curing via silicon bridge. The alkoxysilanes are rigidly connected to the chromophores via Heck reactions or cross-metathesis with vinylalkoxysilanes. Hydrolysis and subsequent condensation yields oligosiloxanes with pendant OPVs, thus greatly improving the film forming capability of these materials well defined chromophores. The connection to cyclosiloxanes and oligosiloxanes has a distinct influence on the electronic spectra of the OPVs in the solid films. Additionally, conjugated systems with high electron affinity like 2,5-diaryl-1,3,4-oxadiazoles are functionalized with alkoxysilane oligomers. These materials are interesting for the preparation of organic-inorganic hybrid materials with luminescent building blocks.
In the last few years an increased interest was devoted to hybrid organic-inorganic multifunctionality molecular materials aiming to obtain synergy between two physical properties. For the particular class of materials combining electrical conductivity and magnetic interactions, it is hoped to achieve magnetic coupling between the localized spin of the inorganic part through the mobile electrons of the organic part via the so-called red interactions. In order to meet this mechanism, we are investigating in our group materials where the two systems interact through space or through a conjugated bridge. We will present in this contribution some of our results according to these ideas: 1. we present materials with coexistence of bulk ferrimagnetism and quantum weak ferromagnetism as well as an evidence from the ESR spectroscopy of the interactions between the p and d electrons. These materials are based on organic donors and paramagnetic coordination complexes with ligands 2. We present novel molecular bricks, namely $[\text{M} \text{II(bdc)2]}][\text{TTFppy}]_2$, M = CuII, M = Fe, bdc = hexahydroura-cetanate, TTFppy = 4(2,4-diaminophenyl)pyridine in which the conducting and the magnetic systems are covalently linked through a conjugated bridge.


3:45 PM Q12.8
NEW INORGANIC ORGANIC OPEN FRAMEWORK
CHALCOGENIDES, Pingyun Feng, Cheng Wang, Xinhai Bu, Nanfeng Zheng, Yugu Li, Department of Chemistry, University of California, Riverside, CA.

The synthesis and characterization of a series of inorganic-organic chalcogenides will be described. These materials have rich compositional and structural diversity including sulfides, selenides, tellurides and their various combinations. Structures typically consist of crystalline inorganic frameworks encapsulating disordered molecular guest molecules. Inorganic frameworks consist of different clusters connected into various topologies. In addition, non-cluster based host-guest frameworks have also been identified. These materials possess various properties ranging from photoluminescence to ion-exchange.

4:00 PM Q12.9

Sol-gel chemistry provides the “nanostructural engineer” with a range of nanosized precursors for the production of thin films tailored properties. In this study, we have investigated the structural evolution of thin titania films prepared from three types of sol-gel precursor:
- Polymers: titania sols, prepared by controlled hydrolysis of titanium butoxide at pH 1;
- Stable nanoparticles (~ 5 nm) prepared by hydrolysis of acetylacetone-modified titanium isopropanoxide and subsequent precipitation at pH 2;
- Ordered oxo-organ titanium (IV) clusters (including $[\text{Ti}_4\text{O}_8]_n[\text{OR}]_m[\text{OOR}]_n$ and $[\text{Ti}_3\text{O}_5]_n[\text{OR}]_m[\text{OOR}]_n$) prepared by controlled hydrolysis of carboxylic acid-modified alkoxides.

Thin titania films (~ 20 nm thick) were deposited on silicon wafers by spin coating, drying at 60°C for 12 hours and subsequent firing at 150-600°C using either conventional furnaces or rapid thermal annealing. The corresponding microstructures were characterised using spectroscopic ellipsometry, atomic force microscopy, X-ray diffraction and cross-sectional transmission electron microscopy. The structure of the oxo-organ titanium (IV) clusters was characterised using single crystal X-ray diffraction and vibrational spectroscopy (FTIR and Raman). The role of precursor chemistry, size and internal structure (particularly oxygen and titanium coordination in the ordered clusters) in mediating the structural evolution and crystallisation behaviour of the films will be discussed in detail.

4:15 PM CONCLUDING REMARKS