

**SYMPOSIUM Q**  
**Hybrid Organic-Inorganic Materials**

April 1 – 5, 2002

**Chairs**

**Richard M. Laine**

Dept of MS&E  
Univ of Michigan  
2114 HH Dow Bldg  
Ann Arbor, MI 48109-2136  
734-764-6203

**Shu Yang**

Lucent Technologies  
Rm 1D-353  
Murray Hill, NJ 07974  
908-582-2806

**Clement Sanchez**

Lab Chimie de la Matere Condensee  
Univ of Pierre-Marie Curie  
LCMC, UPMC, Tour 54 5e tage  
Paris Cedex 05, 75252 FRANCE  
33-14427-5534

**C. Jeffrey Brinker**

Advanced Materials Lab  
Sandia Natl Laboratories  
Albuquerque, NM 87106  
505-272-7627

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\* Invited paper

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

**1:25 PM OPENING REMARKS**

**1:30 PM Q1.1**

ORGANIC/INORGANIC NANOCOMPOSITES BASED ON  
FUNCTIONALIZED PHENYLSILSESQUIOXANES. R.M. Laine, R.  
Tamaki, J. Choi, C. Brick, S-G. Kim, N. Takamura, K. Park,  
Departments of Materials Science and Eng., Chemistry and the  
Macromolecular Science and Eng. Center, University of Michigan,  
Ann Arbor, MI.

Introduction: Our goal is to develop structure-property-processing relationships in nanocomposites prepared using octafunctional silsesquioxanes [(RSiO)<sub>1.5</sub>]<sub>8</sub>, cubes] to establish a complete understanding of the behavior materials that are expected to offer physical properties nonlinearly related to the properties of the component phases. In the studies presented here we have developed cubes with functionalized phenyl groups (R = BrPh, AcylPhenyl, NH<sub>2</sub>Phenyl, etc). These materials provide access to high temperature nanocomposites, can in some instances be melt processed and, also offer access to materials with photonic and electronic as will be discussed here.

References:

1. R.M. Laine, J. Choi, I. Lee, 'Organic-Inorganic Nanocomposites with Completely Defined Interfacial Interactions', Adv. Mater. 13, 800-3 (2001).
2. J. Choi, J. Harcup, A.F. Yee, Q. Zhu, R.M. Laine, 'Organic/Inorganic hybrid composites from cubic silsesquioxanes', J. Am. Chem. Soc. ASAP Article 10.1021/ja0107201S0002-7863 (01)00720-X.

**1:45 PM Q1.2**

HYBRID INORGANIC-ORGANIC PERFORMANCE FLUIDS  
BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES  
(POSS). Rusty L. Blanski, Shawn H. Phillips, Brent Viers, Air Force  
Research Laboratory, Edwards AFB, CA; Justin Leland, ERC Inc  
Edwards AFB, CA.

Performance fluids that operate at high temperature can be useful for many applications including highly efficient automobile engines and jet turbines. One challenging aspect to this project is to increase the use temperature of the performance fluid while maintaining low temperature pourability. One possible solution to this hurdle is to combine the high temperature stability of a silsesquioxane framework with the lubricity of hydrocarbons. Data will be presented on a wide variety of POSS alkyls were synthesized to test the various POSS frameworks for temperature stability and pourability at lower temperatures. Thermal and viscosity data will also be discussed.

**2:00 PM Q1.3**

MOLECULAR DESIGN OF 'SMART' ORGANICALLY-MODIFIED  
SOL-GEL MATERIALS. Mukti S. Rao and Bakul C. Dave,  
Department of Chemistry and Biochemistry, Southern Illinois  
University, Carbondale, IL.

This presentation will focus on the design, synthesis, and stimuli-responsive behavior of organically-modified silicates (ORMOSILS) containing response-active spacer units. The ORMOSILS 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 elaborated. 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  
Chairs: Jean-Francois Gerard and Pedro Gomez-Romero  
Monday Afternoon, April 1, 2002  
Metropolitan II (Argent)

**2:15 PM \*Q2.1**

HYBRID RANDOM LASERS. M. Psyllaki, D. Anglos, S.H.  
Anastasiadis, Institute of Electronic Structure & Laser, FORTH,  
GREECE; R.N. Das and E.P. Giannelis, Department of MS&E,  
Cornell University, Ithaca, NY.

In conventional lasers photons reflected back and forth through a cavity stimulate 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 I will describe our efforts to develop random lasers based on semiconductor particles (ZnO, ZnS, TiO<sub>2</sub>) 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 literally scores of applications for lasers that can literally be painted on. Applications include machine-vision in robotics, in search and rescue operations and in flat panel displays.

**2:45 PM Q2.2**

IN-SITU POLYMERIZATION VS DIRECT POLYMER  
INCORPORATION FOR THE NANOCOMPOSITE PSS/LDH.  
Fabrice Leroux, El Mostafa Moujahid, Jean-Pierre Besse, 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 polystyrene 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 <sup>13</sup>C CP MAS spectroscopy, the in-situ polymerization of vinylbenzene sulfonate (VBS) is confirmed simultaneously by the disappearance of the C=C resonance peak and the presence of -(CH<sub>2</sub>)-. 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 (shielding or not depending of the carbon), 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 macroporous domain associated with a surface area of 60 m<sup>2</sup>/g, whereas these characteristics between the pristine LDH and PSS in-situ polymerized materials are not significantly changed, the distribution ranges in the mesoporous region associated with a surface area of 15 to 20 m<sup>2</sup>/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 features of Freundlich type whereas they are of Langmuir type for (VBS)LDH material. We demonstrate using <sup>27</sup>Al solid state NMR that the in-situ polymerization method gives rise to material more stable in temperature than the other nanocomposite. The most stable 2D 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 NANOCOMPOSITES.  
Bénédicte Lebeau, Laboratoire de Matériaux Minéraux, ENSCMu,  
CNRS, Mulhouse, FRANCE; Nicola T. Whilton, 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 Mg-phyllsilicates were prepared inside a poly(ethylene oxide) (PEO) matrix under quasi non-aqueous conditions. The sol-gel based method involved the precipitation of the smectite-like framework from mixed ethanol/polymer solutions containing organotrialkoxysilane 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-organoclay composites in bulk and films consisting of amino-functionalised magnesium organo-phyllsilicates embedded in PEO matrix have been prepared with different layered inorganic particle loadings. Typically, the molar ratio Si:EO (ethylene oxide unit) was varied from 1:10 to 1:1. X-ray diffraction patterns recorded showed for all samples showed reflections characteristic of crystalline PEO and layered magnesium organosilicate. The intralayer reflection at 2θ~59 (d<sub>060,330</sub> = 1.56-1.57 Å) is characteristic of the 2:1 trioctahedral phyllosilicate structure and was observed in the XRD patterns in all the PEO-magnesium (organo)phyllsilicates synthesized. The presence of this reflection indicated not only the successful formation of the smectite-like structure, but also the ability of the layered inorganic framework to accommodate the presence of

the polymer matrix without losing long-range periodicity. Increasing the inorganic content of the samples resulted in an increase in the intensity of the X-ray reflections characteristic of magnesium organo-phyllsilicates 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 MODELLING STUDIES OF ALUMINO-PHOSPHONATE STRUCTURES.** Paramjit Grewal, Paul Cox, Centre for Molecular Design, University of Portsmouth, UNITED KINGDOM; Julian Gale, Department of Chemistry, Imperial College of Science, London, UNITED KINGDOM; Paul Wright, School of Chemistry, University of St. Andrews, Fife, UNITED KINGDOM.

The mixed inorganic-organic nature of these 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 aluminophosphonate structures AlMePO-1, AlMePO-a, AlMePO-b, AlBzPO-I and AlBzPO-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 attached 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 distributions and to probe the nature of the H<sub>2</sub>O-framework interactions. This is exemplified by the results for AlBzPO-I, 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 -(CH<sub>3</sub>) groups in the two structures investigated, AlMePO-1 and AlMePO-b, are both consistent with rapid rotation of these groups at ambient temperature and compare favourably with the activation energy of -(CH<sub>3</sub>) rotation in AlMePO-b determined via NMR measurements. In contrast, the barrier height for rotation of -(C<sub>6</sub>H<sub>5</sub>) groups in AlBzPO-1 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

Chairs: Joel J.E. Moreau 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 sol-gel processing of amorphous hybrid organic-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 organotrialkoxysilanes 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 polysilsesquioxanes. This will include a survey of synthetic methodologies, processing, properties and applications of these materials.

#### 9:00 AM Q3.2

**ORGANISATION IN ORGANO-POLYSILSESQUIOXANES PREPARED BY SOL-GEL PROCESS AND BY SOLID STATE POLYMERIZATION.** Frédéric Ben, Bruno Boury, Robert Corriu,

Valérie Le Strat, Laboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Montpellier, FRANCE.

Organo-polysilsesquioxanes (NOPS) are silicon-based hybrid materials prepared by Sol-Gel process. Using precursors of the general formula R-[Si(OMe)<sub>3</sub>]<sub>n</sub>, a complete hydrolysis/polycondensation lead ideally to highly cross-linked material. These are currently under investigation for mesoporous material, NLO materials or luminescent materials. For such organo-polysilsesquioxanes we have reported the presence of a short-range organization leading to anisotropic materials. By an alternative approach, performing hydrolysis/polycondensation in the solid state of organo-poly(trichlorosilane), we have prepared organo-polysilsesquioxanes with a long-range organization. We report on the short-range anisotropic organization of the organo-polysilsesquioxanes 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 auto-association during the chemical transformation and mechanical orientations due to the cracks certainly play an important role. As a new alternative, we present the first results on the preparation of Organo-polysilsesquioxanes with various R groups by solid state hydrolysis/polycondensation of organo-poly(trichlorosilane). Both evidences of chemical transformations and of the long-range organization of the solid demonstrate the potentialities of this approach.

#### 9:15 AM Q3.3

**MODEL SYSTEMS FOR HYBRID ORGANIC-INORGANIC MATERIALS DEVELOPMENT.** Thomas A. P. Seery, 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 polymerization from these initiator sites 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 arsenide 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 chemist to follow the progress of a sequence of reactions. With these tools in hand we have prepared hybrids metals, oxides, sulfides and arsenides with hydrocarbon polymers. These polymers include both flexible and semiflexible chains, side chain liquid crystalline polymers and functional polymers. The kinetics of these polymerizations have been followed 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 dispersity

#### 9:30 AM Q3.4

**AZOBENZENE BRIDGED POLYSILSESQUIOXANES.**

John T. Lean, Doug A. Loy, Catalysis and Chemical Technologies, Sandia National Laboratories, Albuquerque, NM.

Bridged polysilsesquioxanes 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 photoisomerization on the overall properties of the hybrid materials. In this study, an azobenzene bridged polysilsesquioxane monomer was prepared from dibromoazobenzene using the Pd-catalyzed Heck reaction. High yields were obtained with Pd(OAc)<sub>2</sub> and P(o-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 materials where it is molecularly dispersed and covalently bonded by two alkoxy silane 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 or thermal geometric isomerization of the azobenzene crosslinking moiety would have on the bulk physical and chemical properties of the materials.

#### 9:45 AM \*Q3.5

**METAL OXIDE-ORGANIC HYBRID MATERIALS BASED ON ORGANOPHOSPHORUS COUPLING AGENTS.** P. Hubert Mutin, André Vioux, University of Montpellier II, Department of Chemistry, Montpellier, FRANCE.

Coupling molecules are required to bind covalently organic groups to an oxide network. Alkoxy silanes have been widely used for coupling with silica, but are much less efficient with metal oxides such as

tania. 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-OR (or M-OH) and P-OX (X = H, Me<sub>3</sub>Si, Et) functions. These condensation reactions allow the preparation of organic-inorganic hybrids, either by sol-gel processing with metal alkoxide precursors or by modification of metal oxide surfaces. Phosphonate coupling molecules, R-P(O)(OX)<sub>2</sub> have been more 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 molecular compounds that are precious structural models of the final hybrid materials. In addition, these compounds are soluble in common organic solvents and contain hydrolyzable alkoxy groups, which makes them potential sol-gel precursors. The metal oxide phosphonate hybrid xerogels were found homogeneous: no phase separation to metal phosphonate and metal oxide occurs, 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 coordination of the P=O groups on Lewis acid sites and, depending on the grafting conditions (concentration, temperature, nature of X), cleavage of M-O-M bonds. The different reactivities of organophosphorus and alkoxysilanes coupling agents make them quite complementary: alkoxysilanes are the best choice in the case of silica, and organophosphorus appear very efficient for metal oxides such as titania, alumina, or zirconia.

SESSION Q4: WELL-DEFINED NANOBUILDING BLOCKS—PRECURSORS FOR HYBRIDS II  
Chairs: Florence Babonneau and Richard M. Laine  
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, Vienna 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 carboxylic acids. The cluster size and shape can be influenced by the reaction conditions. Radical polymerization of small proportions of the clusters (0.5 - 2 mol%) with unsaturated organic co-monomers (methylmethacrylate, acrylic acid, styrene, etc.) results in inorganic-organic hybrid polymers in which the clusters crosslink the polymer chains. The swelling behavior in organic solvents, the thermal decomposition behavior, the dielectric properties and the 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 COPOLYMERIZATION INTO ORGANIC-INORGANIC HYBRIDS. Brent D. Viers, Rene Gonzalez, Timothy Haddad, Shawn Phillips Air Force Research Laboratory, Propulsion 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 (styrenics, acrylics, olefins, etc.) to form organic inorganic hybrid materials. Indeed, the synthetic control that is afforded during the POSS formation and subsequent functionalization can allow 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 'conona' functionalities that are available, and the effect of different coronas on the compatibilization 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. Soles, Sheng Lin-Gibson, Zhi-Gang Wang, Eric K. Lin, NIST Polymers Division, Gaithersburg, MD; Brent D. Viers, Air Force Research Lab, Edwards Air Force Base, CA.

Recently there have been efforts to create inorganic-organic hybrid materials by attaching POSS (polyhedral oligomeric silsesquioxanes) macromers to linear polymers as side or pendant 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 single chain conformational changes in random copolymers as a function of the POSS content in a dilute solution is one of the first step to understanding the bulk structure of these hybrid materials. Specifically, we study the conformation of both poly(methylstyrene-POSS) and poly(norbornyl-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 conformations are then contrast with the spatial correlations of the POSS units, which is easily obtained by small angle X-ray scattering (SAXS). Preliminary SAXS measurements indicate large-scale correlations of the POSS (especially for high molar 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 Matejka, Inst of Macromolecular Chemistry, Acad 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) alkoxysilane-encapped oligomers that are crosslinked by sol-gel polymerization and (b) compact silsesquioxane (SSQO) clusters with epoxy functionalities forming a network by reaction with oligomeric diamines. 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 encapped oligomers is mainly composed of polyhedral cage structures. NMR analysis reveals an agreement between the network and the model. Sol-gel polymerization of a model organotrialkoxysilane 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-glycidioxypropyl)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 diamines to form a network. Structure evolution during network formation, microphase separation and gelation were followed using SAXS and DMA. Mechanical properties and interphase interaction of the cured networks of both types were compared and structure-properties relationships were determined.

Acknowledgement:

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#### SESSION Q5: BIOMATERIALS, BIOGELS, BIOMIMETIC APPROACHES OF MATERIALS

Chairs: Carole C. Perry, Daniel E. Morse, 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 Eglin, Department of Chemistry and Physics, The Nottingham Trent University, Nottingham, UNITED KINGDOM; Saad Ali, Sandra Downes, Group Research Centre, Smith and Nephew Plc, York, UNITED KINGDOM.

Hybrid polyester-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 tetraethylorthosilicate (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

FTIR methods were used to obtain information on the arrangement of the organic polymer in the hybrid materials. A measure of the relative crystallinity of the organic polymer phase gave indirect 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 [2,3] increasing 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 investigated the effect of synthesis variables simultaneously 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 polyester-silica biomaterial for orthopaedic applications.

References:

- [1] D. Tian, Ph. Dubois, R. Jerome. *J. Polym. Sci. Part A: Polym. Chem.*, 1997, 35: 2295-2309.
- [2] S. Jiang, X. Li, L. An, N. Jiang. *Polymer*, 2001, 42: 3901-3907.
- [3] D. Tian, S. Blacher, R. Jerome. *Polymer*, 1999, 40: 951-957.

#### 2:00 PM Q5.2

ASSOCIATION OF SILICA WITH BIOPOLYMERS FOR THE DESIGN OF NEW BIOCOMPOSITES. Thibaud Coradin, Marie-Madeleine Giraud-Guille, Clement Sanchez, Jacques Livage, Chimie de la Matiere Condensee, 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 and to design new bio-inspired materials. Our strategy lies in the association of silica precursors with biopolymers presenting gelation properties. Alginate, 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 revealed to depend on the biopolymer content of the initial solution. The association of alginate and silica was also used to obtain new microcapsules 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-collagene gels. Silica precursors and collagen solutions were mixed in acidic media and simultaneous gelation of both components was induced by ammonia vapour diffusion. Influence of synthesis parameters on silica morphology and collagen organization will be presented.

#### 2:15 PM Q5.3

SYNTHESIS, CHARACTERIZATION AND IN-VITRO RELEASE OF GENTAMICIN FROM CORALLINE HYDROXYAPATITE ACRYLATE GRAFTED ONTO POLY(MMA-GMA) FUNCTIONAL MICROSPHERES FOR OSTEOGENIC AND BONE FILLING MATERIALS. M. Sivakumar, K. Panduranga Rao, Department of MS&E, University of Florida, Gainesville, FL.

Many efforts have been made towards the development of new bone substitute materials. Among these, hydroxyapatite/functional polymer composites have attracted much attention since such composites have some unique advantages over their conventional constituting components. Poly(methyl methacrylate) [PMMA] and its derivatives as an adhesive in bone arthroplasty applications is well known. In the present paper, attempts were made to prepare hydroxyl and epoxy containing PMMA functional [PMMA-F] microspheres using chain transfer agent, mercaptoethonal and glycidyl methacrylate. PMMA-F microspheres were prepared by dispersion polymerization technique and the coralline hydroxyapatite acrylate [CHAA] was synthesized using acryloyl chloride. These prepared CHAA was grafted onto PMMA-F microspheres by polymerization initiation techniques. These grafted ceramic-polymeric composites microspheres were characterized by various techniques such as XRD, FT-IR, TGA, DSC, and EDX. These functional microspheres and grafted materials were analyzed for particle size distribution using particle size analyzer and found to be 260 microns and 300 microns respectively. The optical and SEM micrographs clearly indicated that the CHAA was grafted onto the PMMA-F microspheres. Gentamicin was coupled to the grafted microspheres and in its in-vitro release was carried out in phosphate buffer of pH 7.4 at 37°C. It is aimed to use these biomaterials in orthopaedics particularly in the repair and regeneration of bone and dental.

#### 2:30 PM Q5.4

CONTROL OF HIERARCHICALLY ORDERED POSITIVE AND

NEGATIVE REPLICA OF ORDERED WOOD CELLULAR STRUCTURES BY SOL-GEL MINERALIZATION. Yongsoon Shin, Li-Qiong Wang, Jeong Ho Chang, William, D. Samuels, Larry R. Pederson, Gregory J. Exarhos, Pacific Northwest National Laboratory, Richland, WA; Jun Liu, Sandia National Laboratory, Albuquerque, NM.

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 synthesis and dual templating. 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 an in-situ mineralization of ordered wood cellular structures with surfactant-templated sol-gel at different pHs. At low pH, a silicic acid is coated onto inner surface of wood cellular structure and it penetrates into pores left, where degraded lignin and hemicellulose are leached out, to form a positive replica, while at high pH the precipitating silica particles due to fast condensation clog the cells 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 cellular structures, multi-layered cell walls, pits, vessels well-preserved with positive or negative contrasts, respectively. The surfactant-templated mineralization produces ordered hexagonal nanopores with 20Å in the cell walls after calcination. Such monolithic metal oxides have great potentials in catalysis, separation, bioengineering with a great improvement.

#### 2:45 PM Q5.5

CRYSTALLIZATION OF L-ARGININE PHOSPHATE (LAP) MICROCRYSTALS IN A SILICA SOL-GEL MATRIX. Tanya 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 follows exponential behavior with an enthalpy of solution of 0.68 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 operable over a range of experimental supersaturation and 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 time coincide fairly well 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 PM \*Q5.6

SILICON BIOTECHNOLOGY OFFERS NEW PATHS FOR STRUCTURE-DIRECTING POLYMERIZATION OF SILICA AND SILSESQUOXANES. Daniel E. Morse, Jennifer N. Cha, Katsuhiko Shimizu, Yan Zhou, Jixiang Cao, 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 silica-based composites at low temperatures and near-neutral pH, with a precision of nanostructural control that exceeds present human capabilities. Analyses of the proteins, genes and molecular mechanisms governing the formation of these composites revealed an unanticipated mechanism of synthesis with potential industrial applicability. We found that the silica needles made by a marine sponge are hybrid materials. Each contains an occluded axial filament of protein composed of repeating assemblies of three similar subunits we named "silicateins." Analysis of the purified protein subunits and the cloned silicatein DNAs revealed that the silicateins are highly homologous to a family of hydrolytic enzymes. As predicted from this finding, we discovered that the silicatein filaments catalyze and spatially direct polycondensation to form silica, phenyl- and methyl-silsesquioxane from the corresponding silicon alkoxides at neutral pH and low temperature. Catalytic activity also is exhibited by the silicatein subunits obtained by disaggregation of the protein filaments, and those produced from recombinant DNA templates cloned in bacteria. Genetic engineering was used to produce variants of the silicatein

molecules with substitutions of specific amino acid sidechains. In conjunction with molecular modeling, this allowed us to probe the determinants of catalytic activity and confirm the identification of the amino acid sidechains required for hydrolysis of the silicon alkoxides. From these findings, we then predictively synthesized biomimetic diblock copolypeptides incorporating 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 silica at neutral pH, while simultaneously directing the 3-dimensional structures of the resulting silicon-based composites. We now are exploring paths to harness the structure-directing activity of the silicateins and their biomimetics to produce ordered polysiloxanes and inorganic/organic hybrid materials with enhanced optoelectronic and other physical properties, and to write nanostructural features of silica on silicon chips.

#### 3:45 PM Q5.7

**BIOLOGICALLY-DRIVEN FABRICATION OF A HYBRID ORGANIC/INORGANIC DEVICE.** Rajesh R. Naik, Lawrence L. Brott, Sean M. Kirkpatrick and Morley O. 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 silica-precipitating activity of peptides with a holographic two-photon induced photopolymerization process. The R5 peptide, identified from the diatom *Cylindrotheca fusiformis*, forms silica nanospheres from silicic acid under physiological conditions in vitro. By incorporating these peptides into 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 silane precursor, silica nanospheres are precipitated in the peptide-rich regions resulting in a highly ordered two-dimensional array of silica nanospheres 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 POLYMER-CERAMIC COMPOSITES AS BONE GRAFTS.** Samar Kalita, John Finley, Susmita Bose, Howard Hosick\* and Amit 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 in-growth. The present research is based on development of polymer-ceramic composite using polypropylene (PPE) polymer and tricalcium phosphate (TCP) 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 polymeric materials were mixed under high shear using a torque rheometer. Compounded materials were then extruded to a 1.78mm diameter filament using a single screw extruder. These filaments were used as a feed-stock 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 (OPC-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 vitro studies of PPE-TCP composites having controlled three dimensionally inter-connected 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.** Jack Y. Lu, Amy M. Babb, Vaughn Schauss, Jose Macias, Wilfredo A. Fernandez, Edward E. Kohler and Benjamin J. Biela, Department of Chemistry, University of Houston-Clear Lake, Houston, TX.

Design and Synthesis of functional porous materials represent one of the new areas in materials science and technology. Porous open-framework polymers have shown interesting properties such as molecular separation and pollution prevention in air, liquid and water system, where they can be used as ion exchangers and molecular sieves. Nano-porous materials may be designed based upon the structural information. The desirable nano-porous materials may find their applications in biomedical, catalysis and separation technology. Our exploration in this area has produced novel microporous framework polymers. The synthesis and structure of the new nano-porous metal-organic polymers will be presented. Related Publications:

J.Y. Lu and Babb, A.M. Chem. Commun. 2001, 821. 'An Unprecedented Interpenetrating Structure With Two Covalent-Bonded Open-Framework of Different Dimensionality.' J.Y. Lu, C. Norman, K.A. Abboud and A. Ison, Inorg. Chem. Commun. 2001, 4, 459. 'Crystal Engineering of An Inclusion Coordination Polymer With Cationic Pocket-Like Structure and Its Property to Form Metal-Organic Nanofibers.' J.Y. Lu, K.A. Runnels and C. Norman, Inorg. Chem. 2001, 40, 4516. 'A New Metal-Organic Polymer with Large Grid Acentric Structure Created by Unbalanced Inclusion Species and Its Electrospun Nanofibers'. J.Y. Lu and A.M. Babb Inorg. Chem. 2001, 40, 3261. 'The First Triple-Layer 2-D Coordination Polymer: [Cu3(bpen)(IN)6(H2O)2]'. J.Y. Lu and K.A. Runnels, Inorg. Chem. Commun. 2001, 4, 678. 'An Unprecedented Mixed-Valent-Copper Metal-Organic Polymer Displaying Graphite-Like Properties.'

#### Q6.3

**OXOTANTALUM CLUSTERS AS BUILDING BLOCKS FOR INORGANIC-ORGANIC HYBRID MATERIALS.** Silvia Gross, Guido Kickelbick, Ulrich Schubert, Inst of Metals Chemistry, Vienna Univ of Tech, Vienna, AUSTRIA; Vito Di Noto, Dept of Inorganic Chemistry, Univ of Padova, Padova, ITALY.

Novel organically modified tantalum oxide clusters were prepared via the sol-gel route by reaction of tantalum pentaethoxide with acrylic or methacrylic acid. The clusters, bearing polymerizable methacrylate moieties, were then polymerized with methyl methacrylate or styrene as co-monomers. 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), <sup>13</sup>C MAS NMR and impedance spectroscopy (IS). 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 depolymerization stage is shifted to higher temperature with respect to the undoped polymers. The tantalum cluster based hybrid polymers are very promising dielectric materials owing to the fact that their conductivities are five order of magnitude lower than that of pristine PMMA.

#### Q6.4

**MULTIFUNCTIONAL MATERIALS: 2D CONSTRAINED ELECTRONICALLY CONDUCTIVE POLYMER INTO LDH MATRIX.** El Mostafa Moujahid, Marc Dubois, Fabrice Leroux, Jean-Pierre Besse, Dept of Chemistry, Univ. Blaise Pascal, Aubière, 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 polyaniline (PANI)/ 2D material. In these organic/inorganic materials, the polymer is incorporated to enhance the electronic conductivity, the bidimensional framework provides the stability and the processability. Aniline-3-sulfonate is readily incorporated between the layers of [Cu<sub>2</sub>Cr(OH)<sub>6</sub>] hydroxalcalite type material. Compared to aniline, the presence of the electrophilic function decreases the potential of monomer, although decreasing the conductivity of the polymer in its conductive state, even if the sulfonic acid ring-substituted polyaniline is capable of self-doping. The in-situ polymerization of the monomer induces a decrease of the basal spacing, indicative of a constrained environment for the polymer. The presence of sulfonate polyaniline (SPANI) 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-dependent signal,  $\Delta H_{pp}=32\text{G}$  (293K) associated with  $g=2.0041$ ). 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 sample made by the in-situ polymerization method. Finally, the electrochemical behavior in aprotic solvent is 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 ( $\Delta H_{pp} \approx 1000\text{-}1100\text{ G}$  with  $g=2.0172$ ), whereas it is significantly changed between the oxidation (200mV/Pt) and the reduction (-1200mV/Pt).

#### Q6.5

Transferred to Q10.7.

#### Q6.6

**TIN-BASED HYBRID MATERIALS PRECURSORS OF MESOPOROUS TIN OXIDE.** Bernard Jousseau, Hocine Riague, Thierry Toupance, Laboratoire de Chimie Organique et Organométallique, Université Bordeaux I, Talence, FRANCE; Mohamed Lahcini, 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 trialkynyltins leading to gels upon hydrolysis. The starting materials were obtained by alkylation of the corresponding bridged trichlorotins, where the tins are linked through an alkyl, aryl or benzyl spacer. The bridging configuration of the spacers 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 hydrolysis conditions. Then, the gels were dried and thermolyzed to give micro- or mesoporous tin oxide with high specific area.

#### Q6.7

**MESO-ORDERED SILICA FILMS FORMED BY SUGAR-BASED SURFACTANTS.** Urška Lavrenčič Štangar, Nicola Hüsing, Technische Univ Wien, Inst für Anorganische Chemie, Wien, AUSTRIA.

Sugar-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 surfactants, such as the commercially available alkyl glycosides (e.g. n-octyl  $\beta$ -D-glucopyranoside, n-octyl  $\beta$ -D-galactopyranoside and n-dodecyl  $\beta$ -D-maltopyranoside), are compared with respect to their ability to cooperatively self-assemble in alcoholic silicate solutions. The larger polar head group (maltose) 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 glucose-based surfactant. The inorganic-organic composite 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 glycoside surfactants with alkyl hydrophobic units, some tailor-made glycoside surfactants with poly(dimethyl siloxane) hydrophobic units are also considered for the synthesis of ordered silica films. As a silica source, the prehydrolyzed tetraethoxysilane 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 MONOMER-FREE DENTAL COMPOSITES.** Simone Klapdohr, Norbert Moszner, Thomas Völkel, Volker Rheinberger, Ivoclar Vivadent AG, Schaan, LIECHTENSTEIN.

Organic-inorganic hybrid materials based on functionalized silanes are being used for dental fillings, because of their good mechanical properties, low volume shrinkage and improved abrasion 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 trialkoxysilanes with an amine spacer in the presence of ammonium fluoride. These new silanes 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 succinic or glutaric anhydride with glycerol dimethacrylate resulted in new dimethacrylate-functionalized 3-amidopropylsilanes. Hydrolysis and condensation of these silanes were carried out in the presence of 0.5 N HCl and have been studied by  $^{29}\text{Si}$  NMR spectroscopy. Diluent-free composites have been obtained by photopolymerization of the polycondensates and their mixtures in the presence of camphorquinone and ethyl 4-(dimethylamino)benzoate with visible light. Further improvement of the mechanical properties of the polycondensates was obtained by incorporation of dispersed  $\text{SiO}_2$  nanoparticles and well defined zirconium clusters coordinated by 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 10800 MPa was obtained.

#### Q6.9

**HELICAL LIPID - SILICA MESOSTRUCTURES.** Annela Seddon, Christine Spickermann, 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 diacetylinic phosphatidylcholine have been extensively studied as they provide a valuable insight into molecular self-assembly. In this work, diacetylinic phosphatidylcholine 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 photopolymerisation properties, turning blue due to ene-yne polymerisation of the lipid diacetylinic backbone. Significantly, this behaviour is not observed when preformed mineralised tubules are placed in the reaction medium, suggesting that the presence of intercalated silica within the in-situ coated tubules facilitates topotactic polymerisation. The mineralised tubules were studied by electron microscopy, powder x-ray diffraction, IR, diffuse reflectance UV/Vis and Raman spectroscopy.

#### Q6.10

**THE EFFECTS OF ENHANCED INTERACTION ON INORGANIC/ORGANIC HYBRID SYSTEM.** Seungpyo Hong, Soon Man Hong, Seung Sang Hwang, Hyong-Jun Kim, Tae Gyoung Hwang, Korea Inst of Sci & Tech, Polymer Hybrids Research Ctr, Seoul, KOREA; Eung Chan Lee, Intersilicone Co Ltd, Seoul, KOREA.

New polymethylphenylsilsesquioxanes (PMPSQs) with highly regulated structure were hybridized with organic flexible polymers. Nanoscaled surface images of these hybrids are observed by Atomic force microscopy (AFM). The prepared pure PMPSQ spin-coated film and PMPSQ/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 tens of nanometers. No self-aggregation of each phase occurred in the range of organic portion from 10 to 30 wt%. As interaction such as inter-hydroxyl and aromatic-aromatic interaction increases, more uniform phase distribution and smaller domain size on continuous inorganic matrix are obtained. The effects of polar groups were also investigated 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

**DIELECTRIC PROPERTIES AND MORPHOLOGY OF NANOFOAMED POLY(METHYLPHENYLSILSESQUIOXANE)S.** Eung Chan Lee, Intersilicone Co Ltd, Seoul, KOREA; Seungpyo Hong, Tae Gyoung Hwang, Seung Sang Hwang, Soon Man Hong, Soo Hyun Kim, Korea Inst of Science and Technology, Polymer Hybrids Research Center, Seoul, KOREA.

Inorganic/organic hybridization has greatly attracted scientific and industrial interests. The organic dispersed inorganic matrix would be applied to innumerable industrial fields such as microelectronic packaging materials, optical devices, liquid crystal display elements, magnetic recording media, and carcinostatic drugs. We hybridized polymethylphenylsilsesquioxane (PMPSQ) and Poly-D,L-lactic acid-1,6-hexanediol(PDLLA-1,6-hexanediol). Prepared inorganic/organic hybrids are investigated in terms of nano-scaled morphology by atomic force microscopy (AFM). In particular, the inorganic/organic hybrid material based on polyorganosilsesquioxane (PSSQ) is one of the most promising candidates for low K materials. The hybrids exhibited excellent film coatibility, adhesion, and planarity. Nanofoaming process carried out at optimized condition. The nanofoamed PMPSQ thin films were studied by morphologies and

dielectric properties. As increase of PDLA-1,6-hexanediol resulting air-void, dielectric constants of the films were significantly lowered. Particularly, in the case of PMPSQ/PDLA-1,6-hexanediol (85/15) hybrid films showed not only the most uniform nanofoam 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 Mutin, Gilles Guerrero, André Vioux, 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 metals, phosphine-alkoxysilanes such as  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  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  $\text{TiO}_2$  and  $\text{MgO}$  [1]. We are currently investigating the use of organophosphorus compounds as coupling molecules. These molecules appear complementary of alkoxysilanes and they are well suited to the preparation of covalent  $\text{TiO}_2$ -based hybrid materials by sol-gel processing [2] or surface modification [3]. In this paper we report the sol-gel immobilization of phosphines and their Pd and Pt complexes in  $\text{TiO}_2$  and  $\text{ZrO}_2$  matrices, using  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}(\text{O})(\text{OSiMe}_3)_2$  and  $\text{Ph}_2\text{P}-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{OSiMe}_3)_2$  coupling agents. The hybrid solids were characterized by elemental analysis, solid-state MAS NMR spectroscopy, surface area measurements, XRD, and complexation-decomplexation experiments.

[1] Ch. Merckle, Blümel, J. Chem. Mater. 2001, 13, 3617.

[2] G. Guerrero, P.H. Mutin, A. Vioux, Chem. Mater. 2000, 12, 1268.

[3] G. Guerrero, P.H. Mutin, A. Vioux, Chem. Mater. 2001, Web Release Date: October 16, 2001.

#### Q6.13

**SOLUBLE METHANOFULLERENES AND FULLERODENDRIMERS IN SOL-GEL MESOPOROUS SILICA HOST MATRICES FOR REVERSE SATURABLE OPTICAL ABSORPTION.** J.L. Rehspringer, Y. Rio, D. Felder, J.F. Nierengarten, B. Hönerlage, Institute de Physique et Chimie des Matériaux de Strasbourg, Strasbourg, FRANCE; G. Kopitkovas, Institut of Materials Science and Applied Research, Vilnius University, LITHUANIA; A. Chugreev, Ioffe Physical-Technical Institut, St. Petersburg, RUSSIA.

The non linear optical properties of the fullerene C60 have been intensively 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 synthesize highly soluble compounds. The mesoporous silica host matrices are prepared by following a TMOS acidic hydrolysis with formamide. Several parameters ruling the pore size were investigated. After a heat-treatment at 600°C the pore size is measured by nitrogen physisorption. A wide range of mesoporous samples is obtained (pore sizes from 2-4 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 fullerodendrimers with peripheral triethyleneglycol chains. The preparation scheme will be described. The methanofullerenes are dissolved in THF-Water-Ammonia solutions and added to the sol before gelation. The fullerodendrimers are infiltrated into mesoporous silica using soaking process 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 singlet-state lifetime is observed compared to C60 in solution. This is attributed to micellar aggregates. The interaction of the neighboring C60-cores shortens the singlet lifetime by solid-state effects. Concerning fullerodendrimers they show a similar singlet-state cross section and singlet lifetime, but higher quantum efficiency (singlet to triplet). Their properties let us think that they can be of high interest for optical protective coating.

#### Q6.14

**STRUCTURAL CHARACTERIZATION OF PERIODIC POROUS ORGANOSILICA POWDERS AND THIN FILMS.** V. Goletto, B. Alonso, D. Grosso, G. Trimmel, F. Babonneau, Chimie de la Matière Condensée, UPMC, Paris, FRANCE; M. Impérat, P.A. Albouy, Physique des Solides, Université Paris-Sud, Orsay, FRANCE; M. Wong-Chi-Man, ENSC Montpellier, FRANCE.

Using surfactant-mediated synthesis, a large variety of organic functions can be incorporated in silica-based nanoporous materials in

order to create original materials that can find applications in fields ranging from adsorption, ion exchange, catalysis and sensing technology to nanoelectronics. The organic functions can be easily introduced during the synthesis of the templated network, either as pendant or bridging groups using two families of organoalkoxysilanes,  $(\text{RSi}(\text{OEt})_3)$  and  $(\text{OEt})_2\text{Si-R-Si}(\text{OEt})_2$  respectively. Various powdered samples with hexagonal and cubic symmetries have been synthesized introducing alkyl or aryl moieties bonded to Si using methyltriethoxysilane, bis(triethoxysilyl)ethene phenyltriethoxysilane, 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 1,3,5-tris(triethoxysilyl)benzene in the presence of cetyltrimethylammonium bromide. Their detailed structural characterization have been performed by means of XRD with synchrotron radiation, one and two-dimensional multinuclear MAS-NMR and adsorption-desorption experiments. Then the synthesis was extended to dip-coated thin films using evaporation induced self-assembly.

#### Q6.15

**INDUCED MICELLIZATION OF HYDROPHILIC DIBLOCK COPOLYMERS.** Corine Gerardin, CNRS-Ecole Nationale Supérieure de Chimie, Montpellier, FRANCE; Martin In, Université Montpellier II, Montpellier, FRANCE; Mathieu Joanicot, CNRS Rhodia 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 polyacrylamide (PAM), and does not interact with inorganic entities; the other block is a polyelectrolyte, it is anionic, such as sodium polyacrylate (PAA). The polymers self-assemble in the presence of positively charged inorganic species due to complexation of the inorganic ions by the anionic block. Mixing PAA-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  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ , or polycationic clusters such as  $\text{Al}_{13}^{7+}$  and  $\text{Al}_{30}^{18+}$ . 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 star-shaped objects formed. The core of the object is constituted by the complex and the neutral polymeric blocks form 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 atom and the pH of the solutions. Finally, the aggregates have shown to be adjustable precursors for the formation of colloidal suspensions of metal hydrolysis products.

#### Q6.16

**BIOMIMETIC SYNTHESIS OF SILVER NANOPARTICLES.** Rajesh Naik, Sarah Stringer, Sharon Jones & Morley 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 led 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<sup>1</sup>. 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 expressed as a fusion with a phage 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 displaying 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 nanocrystals, 40-60nm in size, from a dilute solution of silver nitrate ( $\text{AgNO}_3$ ). 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:

1. Klaus-Joerger et al., Trends Biotechnol 19, 15-20 (2001).

#### Q6.17

**OLIGO(PHENYLENEVINYLENE)S WITH REACTIVE SIDE**



#### CHAINS: AMINE- AND AMIDE BOUND ALKOXYSILANES.

Heiner Detert, Erli Sugiono, Johannes Gutenberg University, Mainz, GERMANY.

Strongly luminescent oligo(phenylenevinylene) chromophores with monodisperse chain lengths are connected via short spacers containing a secondary amine or amide with di- and triethoxysilane groups. The alkoxy silanes can be hydrolysed and condensed to cyclic and linear oligomers with high film forming capability and are also interesting functional units for hybrid materials for electrooptical applications. The luminescence properties in the solid state are influenced by hydrogen bonding of the amides resulting in strong hypsochromic shifts. This poster presents the synthesis of the title compounds, their oligomerisation and the electronic spectra in solution and in the solid state.

#### Q6.18

Abstract Withdrawn.

#### Q6.19

INVESTIGATION OF NLO-DYE/METAL ALKOXIDE SOL-GEL PRECURSOR INTERACTIONS. Bénédicte Lebeau, Laboratoire de Matériaux Minéraux, CNRS UMR 7016, ENSCMu, Mulhouse, FRANCE; Clément Sanchez, Laboratoire de Chimie de la Matière Condensée, CNRS UMR 7574, UPMC, Paris, FRANCE.

The optical property changes of the nonlinear optical (NLO) dye (4-(amino-N,N-diethanol)-2-methyl-4'-nitroazobenzene), named Red17, induced by interactions with different metallo-organic sol-gel precursors  $M(OR)_n$  ( $M = Ti, Zr, Si$  and  $Sn$ ;  $R = C_n H_{2n+1}$ ) have been investigated. Because of its very efficient quadratic hyperpolarizability ( $\beta(0)$  (Red17) =  $55.10^{-30}$  esu), the Red17 is a suitable dye to be embedded within sol-gel matrices to produce hybrid, organic-inorganic, optical devices with NLO properties. In such materials, strong interactions between the dye and the host matrix are required to maintain the dye anisotropic alignment. However, the optical efficiency of the Red17-doped sol-gel material depends on the optical properties of the NLO dye that are very sensitive to the chemical and structural change (viscosity, polarity, acidity) of its environment. Optical properties of Red17 were first studied in solvents with different polarities. Optical properties and structural changes of Red 17 were characterized by optical spectroscopic technique and  $^1H$  liquid state NMR, respectively. A bathochromic shift of 50 nm was observed by UV-vis absorption spectroscopy from benzene ( $\lambda_{max} = 470$  nm) to dimethylsulfoxide (DMSO;  $\lambda_{max} = 520$  nm). This important shift was attributed to the strong polarity of DMSO favoring the formation of hydrogen bonds between the sulfoxide group and the hydroxyl groups of the Red17. In THF, the presence of titanium, zirconium or tin alkoxides make strong modifications in the UV-vis absorption spectrum of the Red17 in THF. On the contrary, when the Red17 is grafted to alkoxy silyl groups, only minor modifications were observed. These modifications were found to be due to Lewis acid-base type interaction between the Red 17 and the metal alkoxide.

#### Q6.20

PROCESSING AND PROPERTIES OF NANOCRYSTALLINE BARIUM TITANATE/ORGANIC HYBRID. Toshinobu Yogo, Reimon Fukuzawa, Wataru Sakamoto, Shin-ichi Hirano, Nagoya Univ, Center for Integrated Res in Sci and Eng, Dept of Applied Chem, Nagoya, JAPAN.

Nanocrystalline particle/organic hybrids have been receiving growing attentions as new inorganic/organic materials. This paper describes the processing of nano-sized barium titanate/organic hybrid from metal-organic precursor. Barium titanate (BT) precursor was prepared from barium metal, titanium isopropoxide and organic modifiers. Several kinds of organic compounds including functional groups were introduced to BT precursor. The structure of the BT precursor was analyzed by IR and NMR spectroscopy. The precursor was found to be a double metal-organic in solution. The precursor was hydrolyzed under controlled reaction conditions. The formation conditions of nano-sized BT particles were investigated. The nanocrystalline particles in the organic matrix were analyzed by SAD, EDX and XRD. The particle size was dependent upon the hydrolysis conditions. The electro-rheological (ER) properties of the hybrid were measured. The ER properties were found to depend upon the functional group of organic modifiers. The dielectric properties of the hybrid were also evaluated.

#### Q6.21

PREPARATION OF A SILICON OXIMIDE GEL VIA A NON-AQUEOUS SOL-GEL ROUTE. Fei Cheng, John S. Bradley, Department of Chemistry, University of Hull, Hull, UNITED KINGDOM; Frederic Lefebvre, Laboratoire de Chimie Organometallique de Surface, Cedex, FRANCE.

The sol-gel 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 sol-gel preparation of a high surface area silicon diimide gel by the acid catalyzed ammonolysis of tris(dimethylamino)silylamine ( $(Me_2N)_3SiNH_2$  (TDSA)).<sup>1</sup> In this work we report a preparation of a high surface area silicon oximino gel via a new non-aqueous sol-gel process based on formamide as the gelling agent for TDSA, and the pyrolytic conversion of the gel to silicon oxynitride. The reaction in N,N-dimethylformamide between TDSA and formamide in a 1:2 molar ratio at 50°C for 12 h gave a transparent compact gel. After washing with THF followed by drying under reduced pressure, a translucent rigid xerogel was obtained. The  $^{29}Si$  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  $SiN_xO_{4-x}$  species. The  $^{13}C$  CP-MAS NMR analysis showed the presence of C=N groups (-157.7 ppm) and N-CH<sub>3</sub> groups (-38.1 and -32.2 ppm). A broad band at 932-1185  $cm^{-1}$  ascribed to Si-O and Si-N and a strong band at 1661  $cm^{-1}$  ascribed to C=N showed in the IR spectrum, consistent with the NMR results. The low intensity bands from 2804 to 2993  $cm^{-1}$  and from 3240 to 3454  $cm^{-1}$  can be assigned to CH and NH groups. These spectral features suggested that the gel comprises an oximino-silicon network  $[SiO(CH)=NSi]_x$  containing small amounts of residual  $NMe_2$  and NH groups. The gel exhibited a microporous structure with a BET surface area of 339  $m^2/g$ . Pyrolysis of the gel under  $N_2$  up to 1485°C gave a black amorphous silicon oxynitride.

<sup>1</sup> R. Rovai, C.W. Lehmann and J.S. Bradley, *Angew.Chem.Int.Ed.*, **38**, 2036 (1999).

#### Q6.22

MAGNETIC SOL-GEL DERIVED POLY(OXYETHYLENE)-SILOXANE NANOHYBRIDS. V.S. Amaral, L.D. Carlos, N.J.O. Silva, Dep. de Física, Univ. de Aveiro, Aveiro, PORTUGAL; V. de Zea Bermudez, Dep. de Química, Univ. de Tras-os Montes e Alto Douro Vila Real, PORTUGAL; K. Dahmouche, C.V. Santilli, Inst. de Química/UNESP, Araraquara, BRAZIL; A.F. Craievich, Inst. de Física/USP, Sao Paulo-SP, BRAZIL; F. Palacio Inst. de Ciencia de Materiales de Aragon, CSIC - Univ. de Zaragoza, Zaragoza, SPAIN.

The magnetic and structural properties of sol-gel derived organic/inorganic nanocomposites doped with Fe(II), Fe(III), Nd(III) and Eu(III) are discussed. These hybrids consist of poly(oxyethylene)-based chains grafted onto siloxane nanodomains by urea cross-linkages. Small angle X-ray scattering for undoped hybrids shows the presence of a well-defined peak attributed to the existence of a spatial correlation of siloxane domains embedded in the polymer matrix. The siloxane particle radius and the interparticle distance are  $7 \pm 1$  and  $40 \pm 2$  Å, respectively. For the doped-nanocomposites the ion-first coordination shell varies drastically with the ion concentration. For compositions up to 5% in mass ions interact with the carbonyl-type oxygens of the urea cross-links at the organic/inorganic interface. Above 10% all the available urea groups are saturated and the coordination at the polymer ether-oxygens is favoured [1]. Magnetic susceptibility was measured in zero-field-cooling and field-cooling procedures.  $Eu^{3+}$ -doped samples ( $J=0$ ) show thermal irreversibility effects up to 150K [2].  $Nd^{3+}$ -doped hybrids show larger magnetic signal ( $J=9/2$ ) with much smaller 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  $Eu^{3+}$  magnetic moment is due to excited states ( $J > 0$ ), influenced by crystal field.  $Fe^{3+}$ -doped hybrids show thermal magnetic irreversibility below 40K and the high temperature behaviour is paramagnetic with antiferromagnetic interactions. The  $Nel$  temperatures increase with  $Fe^{3+}$  concentration up to 16K for the highest concentration. On the other hand,  $Fe^{2+}$ -doped samples do not present thermal irreversibility and the high temperature behaviour is that of a simple paramagnet.

[1] K. Dahmouche, L.D. Carlos, V. de Zea Bermudez, R.A. Sá Ferreira, A.P. Passos de Almeida, C.V. Santilli, A.F. Craievich, J. Mater. Chem., **12**, 2001.

[2] V.S. Amaral, L.D. Carlos, V. de Zea Bermudez, IEEE Transactions on Magnetics, **37**, 2935 (2001).

#### Q6.23

PREPARATION AND CHARACTERIZATION OF ACRYLIC POLYMER TITANIA HYBRID. A STUDY OF ORGANIC-INORGANIC INTERACTIONS IN HYBRID MATERIALS BY MICRO-HARDNESS VICKERS. Van Nhan Nguyen, Francois Xavier Perrin and Jean-Louis Vernet, Laboratoire de Chimie Appliquée Université de Toulon et du Var, FRANCE.

In-situ sol-gel process has been used to prepare the hybrid inorganic-organic based on a methyl methacrylate (MMA)-n-butyl methacrylate

(n-BMA)-methacrylic (MA) terpolymer in the presence of tetrabutyltitanate. The whole hydrolysis-condensation process results in homogeneous and semi-transparent films with amounts of titania ranging from 4.5 to 22%. The characterization of free films was realized by various experimental methods. Infra-red spectroscopy results show that : COOTi bonds are formed and the chelating ones stable up to 200°C. Solvent extraction results proved the strong interaction between the polymer and the inorganic phase through COOTi bonds. Mechanical properties of the hybrid films have also been investigated through dynamic mechanical thermal analysis. The results show that the tensile properties of the composites are strongly enhanced above the glass transition temperature (T<sub>g</sub>) of the polymer. Below T<sub>g</sub>, the tensile properties are not significantly affected. The micro-hardness measurements used in this study allowed us to understand the contribution of the inorganic part (phase TiO<sub>2</sub>) to the mechanical properties of the polymer. The creep of polymer has been studied by the hardness measurements at various temperatures and under various indentation times. The thermal expansion coefficient of hybrid materials was also found from temperature-hardness relation. The mineral constituent leads an important increase of the hardness and limits, in a significant way, the creep of polymer.

#### Q6.24

INCORPORATION OF EUROPIUM (III) β-DIKETONATE COMPLEXES IN THE INTERLAYER SPACING OF α-ZIRCONIUM PHOSPHATE VIA PENDANT AMINO GROUPS. Shanez Tlemsani, Anne-Christine Franville, Daniel Zambon, Rachid Mahiou, Université Blaise Pascal and ENSCCF, Laboratoire des Matériaux Inorganiques, UMR-CNRS 6002, 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 the studies concerning these luminescent hybrid materials are related to 3D amorphous networks such as silica or transition metal oxides whereas very few has yet been reported on bidimensionnal 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 lanthanide β-diketonates 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 acido-basic exchange mechanism used here for insertion involves reactions between pendant phosphonic acid groups and amino-derivatized dibenzoylmethane 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 structure, i.e. the Ln<sup>3+</sup> maximum stoichiometry that could be reached, the interlayer spacing value or the geometrical arrangement of the organic derivatives within the layered structure. The techniques that are used to characterize the final intercalated materials as well as the intermediate compounds include XRD, infrared and <sup>13</sup>C/<sup>31</sup>P NMR spectroscopies. The cation local surroundings are also investigated by Time Resolved Spectroscopy using Eu<sup>3+</sup> as an optical structural probe.

#### Q6.25

SYNTHESIS AND CHARACTERISATION OF TRIOCTAHEDRAL ORGANO PHYLLOSILICATES. Maguy Jaber<sup>a</sup>, Benedicte Lebeau<sup>a</sup>, Jocelyne Brendle<sup>a</sup>, Ronan Le Dred<sup>a</sup>, Melanie Roux<sup>a</sup>, and Joseph Dentzer<sup>b</sup>. <sup>a</sup>Laboratoire de Matériaux Minéraux, UMR-A 7016, Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace, Mulhouse, FRANCE. <sup>b</sup>Institut de Chimie des Surfaces et Interfaces-CNRS, Mulhouse, FRANCE.

Hybrid materials like organo-phyllsilicates exhibit new properties which make them potential candidates for many industrial applications as rubber reinforcement, environmental barriers, 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 soft conditions (room temperature) using octyl-triethoxysilane as the silica source, aluminum acetylacetonate as the alumina source, magnesium nitrate and sodium hydroxide. These hybrid materials belong to the 2:1 trioctahedral phyllosilicates family with inorganic compositions close to the saponite. The ratio of Al (x) could be varied between 0 and 0.33. The X-Ray diffraction patterns are in agreement with layered trioctahedral structure (presence of the (001) peak series and the (060) peak). The high d<sub>001</sub> spacing values (2.4-2.6 nm) can be related to the octyl chains present in the interlayer space. DRIFT and <sup>13</sup>C NMR spectra indicate that the Si-C

bonds are intact and siloxanes are fully hydrolysed giving SiOAl and SiOMg bonds. <sup>27</sup>Al and <sup>29</sup>Si NMR were carried out in order to determine the repartition of the different elements in the layer: Al substitutes for Si in the tetrahedral layer and for Mg in the octahedral one. These results were completed by elementary analysis. The DTA-TG results shows that the organic matter start to decompose in air above 250°C but its complete removal needs temperatures higher than 800°C. The aspect of the materials depends on the value of x; it varies from greasy, waxy, waxy powdery and finally powdery. The hydrophilicity of the solids being strongly depending on the aluminum content. The study of the nature of the dispersed particles (elementary sheets or aggregates) is under progress.

#### Q6.26

RATIONAL SYNTHESIS OF MESOPOROUS ALUMINIUM PHOSPHATES. Michael Tiemann<sup>1,2</sup> and Michael Fröba<sup>1,3</sup>. <sup>1</sup>Institute of Inorganic and Applied Chemistry, University of Hamburg, GERMANY. <sup>2</sup>Recent address: Department of Physical Chemistry, Åbo Akademi University, FINLAND. <sup>3</sup>Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University Giessen, GERMANY.

Mesostructured aluminium phosphates with a variety of structural properties have been synthesised by utilisation of supramolecular structure-directors. A variety of synthetic procedures have been applied, including the choice of various kinds of amphiphiles (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. aluminium oxides or alkoxides and phosphoric acid. In general, the exact stoichiometric composition of the products has turned out to be difficult to control; the relative 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 AlPO<sub>4</sub> network and/or the formation of undesired by-products, such as aluminium oxide species. We report on the synthesis of mesoporous aluminium phosphates from a single-source molecular precursor with a pre-defined AlPO<sub>4</sub> stoichiometry and short-range structure. All products exhibit a strict 1:1 molar ratio of Al:P, 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 m<sup>2</sup>/g. Further characterisation includes powder XRD, <sup>27</sup>Al and <sup>31</sup>P solid state NMR, and IR spectroscopy.

#### Q6.27

A GENERIC SYNTHESIS ROUTE FOR MATRIX ASSISTED SELF-ASSEMBLY OF METAL-OXO CLUSTERS IN ORGANOSILICA SOL-GELS. Mukti S. Rao and Bakul 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 assists the formation of metal-oxo clusters. The metal-ligand interactions can be tuned by change in external environment such that: a) under overload metal ion concentrations, the sol-gel matrix sequesters the metal ions to promote the growth of 4-7 nm size metal-oxo clusters within the porous structure of the matrix, b) a change in pH releases the metal ions from the bound metal-oxo clusters, thereby making the sol-gel matrix behave as ferritin-apo-ferritin analogues. Evidence of the metal-ligand interactions will be shown using UV-Vis, FTIR, TEM, AES and EDXA data.

#### Q6.28

TITANIA HOMOGENEOUSLY DISTRIBUTED WITHIN THE SILICA WALLS OF MESOSTRUCTURED FILMS. Beatrice Launay, Guido Kickelbick, Nicola Huesing, 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 alkoxide precursors. For example, titanium tetraisopropoxide is well known to hydrolyze faster than silicon alkoxide. For a good control over the morphology of the resulting materials, it is necessary to slow down the reactivity of this transition metal alkoxide. In this work, a new precursor based on the ligand-assisted templating approach was synthesized by reaction of titanium alkoxide with a PEO based surfactant molecule (Brij 56 or Brij 92). The formed coordination compound was used as structure-directing agent in a sol containing a silica source, ethanol, water and hydrochloric acid with varied ratios of Si/Ti-Brij 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 retaining the porous structure. The silica-titania material was characterized by X-ray diffraction, different spectroscopic techniques, nitrogen sorption and transmission electron microscopy (TEM). Additionally, the catalytic activity of the titania-silica material was investigated.

#### Q6.29

**MATRIX-ASSISTED FORMATION OF METAL NANOPARTICLES IN ORGANOSILICA SOL-GELS.** Sandie H. Cheung and Bakul C. Dave, 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 nanoclusters 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, HRTEM and EDX data. Finally, the role of the matrix in the assembly of metal sites in the pores of the organosilica sol-gel will be discussed.

#### Q6.30

**VISCOELASTIC AND MECHANICAL PROPERTIES OF POLYIMIDE-CLAY NANOCOMPOSITES.** Mohamed O Abdalla, Sharee Small and Derrick Dean Tuskegee-Center for Advanced Materials (T-CAM), Tuskegee University, Tuskegee, AL.

Polyimide-clay hybrids were prepared by blending a solution of PMR-15 in methanol and two different clay loadings (2 and 5 wt. %) of PGV (an unmodified Na<sup>+</sup>-montmorillonite (MMT)) and three organically modified-MMT (OMMT). Two of the OMMT (denoted PGVC<sub>11</sub>NH<sub>2</sub>COOH, PGVC<sub>12</sub>NH<sub>2</sub>) were prepared by surface treatment of PGV with ammonium chloride salt of a primary amine (dodecylamine) and an amino acid (11-aminoundecanoic acid). The third OMMT (Closite-30B) was obtained commercially. The B-Stage 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 loss modulus (E'') of all 2.5 wt. % clay loading nanocomposites in comparison with the neat polyimide. Increasing the clay loading to 5 wt. % decreased both the E' and E'' of the nanocomposites (except the Closite-30B nanocomposite). The glass transition temperatures of 2.5 wt. % nanocomposites were higher than the neat polyimide. A decrease in the thermal expansion coefficient was observed only for the PGV/PMR-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 polyimide. This trend in the tensile properties was not observed for the 5 wt. % nanocomposites. TGA showed slight improvement in the decomposition temperatures of the PGVC<sub>11</sub>NH<sub>2</sub>COOH and Closite-30B/PMR-15 nanocomposites (2.5 wt. %) in comparison with the neat polyimide. While the PGV and PGVC<sub>12</sub>NH<sub>2</sub>/PMR-15 nanocomposites showed poorer thermal stability than the neat PMR-15.

#### Q6.31

**ENERGY TRANSFER BETWEEN EUROPIUM AND RHODAMINE 700 IN MESOSTRUCTURED SOL-GEL THIN FILMS.** Payam 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 guided toward the silicate region of the film, and rhodamine 700 was partitioned 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-Wuk Lee, Chuanbin 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 multi-length scale composite material using genetically engineered M13 bacteriophage and ZnS nanocrystals. The

bacteriophage, which formed the basis of the self-ordering system, were selected to possess a specific recognition moiety for ZnS crystal surfaces. The bacteriophage were 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 ca. 72 μm domains continuous over several centimeters. In addition, suspensions were prepared in which the lyotropic 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 moiety as well as a liquid crystalline self-ordering system can organize organic-inorganic hybrid materials.

#### Q6.33

**METALLIC NANOPARTICLES FROM SINGLE POLYELECTROLYTE MOLECULES.** Anna Gorodyska, Anton Kiri, Sergej Minko, Manfred Stamm, Institut fuer Polymerforschung Dresden, Dept Physical Chemistry and Physics of Polymers, Dresden, GERMANY.

The adsorption behaviour 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 20nm in length and 5nm 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.** Sang Il Seok, Bok Yeop Ahn, Joo Hyeun Kim and Tae Soo Suh, Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, KOREA.

Microencapsulation is an important technique for encapsulating oil droplets within a capsule. The most widely used application of these microcapsules is the controlled or sustained release of the encapsulated active agent. The functional performance and defined permeability of the microcapsule depend on the morphology, size, and the pore structures of shell, etc. In this study, organically modified silicate (ORMOSIL) glasses were used as wall materials for immediately-, gradually- or non-releasing of the encapsulated oil. Organically modified silicate glasses were prepared by the hydrolysis and co-condensation of appropriate inorganic and organosilicon precursors such as TEOS (tetraethoxyorthosilicate) and MTMS (methyltrimethoxysilane), and followed by sol-gel reaction. The local chemical structure of ORMOSIL was characterized by FT-IR, <sup>29</sup>Si-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 TITANIA BY NON-PHOSPHATE SURFACTANT TEMPLATING.** Yuung-Ching Sheen, Guang-Way Jang, Ming-Jyh Chang, Shyue-Ming Jang, Shin-Hung Yau, Ya-Hui Lin, Jian-Yi Hong, Ling-Meei Tsay 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 amount 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. Mesoporous titania was successfully prepared at our laboratories using amine surfactant as a template. The surfactant template can be removed by solvent extraction or calcination techniques to form a high surface area mesoporous Titania (>600 m<sup>2</sup>/g). The correlation between synthesis conditions and the metal oxide properties was investigated. The interaction between titanium alkoxide and the surfactant was characterized by NMR. The as synthesized mesoporous Titania 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 Franville, Université Blaise Pascal and ENSCCF, Laboratoire des Matériaux Inorganiques UMR-CNRS 6002, Aubière, FRANCE; Bruce Dunn, UCLA, Dept of MS&E, 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 but the use of such systems in the field of optics is only emerging. Compared to amorphous silica gels, some additional benefits of an 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 orientation of fluorescent species within mesostructures, in 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 one non-silylated, leading respectively to a covalent attachment of the chelate to the siloxane framework and to its 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 own effect of the mesoscopic ordering is investigated by comparing the optical properties of the hexagonally arranged materials to those of amorphous films.

### Q6.37

**FUNCTIONALIZED PHENYLSILSESQUIOXANES AS NANOCONSTRUCTION SITES.** R.M. Laine, R. Tamaki, J. Choi, C. Brick, S-G. Kim, N. Takamura, K. Park, Depts of MS&E., Chemistry and Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, MI.

**Introduction:** We have recently discovered a way to functionalize octaphenyl-silsesquioxane. Thus, we have found it possible to prepare  $[(\text{ArSiO})_{1.5}]_8$ , cubes] where R = BrPh, AcylPhenyl, NH<sub>2</sub>Phenyl, etc). These functionalized cubes are 1.2-1.4 nm in diameter and offer rigid scaffolds for nanoconstruction projects. We discuss here octa-aminophenyl cube and its derivatives, and their utility in developing new, high temperature materials.

**References:**

1. R.M. Laine, J. Choi, I. Lee, 'Organic-Inorganic Nanocomposites with Completely Defined Interfacial Interactions,' *Adv. Mater.* 13, 800-3 (2001).
2. J. Choi, J. Harcup, A.F. Yee, Q. Zhu, R.M. Laine, 'Organic/inorganic hybrid composites from cubic silsesquioxanes,' *J. Am. Chem. Soc. ASAP Article* 10.1021/ja0107201S0002-7863 (01)00720-X.

### Q6.38

**REGULATION OF ELECTRONIC COUPLING AND OPTICAL PROPERTIES OF DENDRIMER-ENCAPSULATED METAL NANOPARTICLES.** J. Zheng, M.S. Stevenson, 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 upon electronic coupling between individual nanoparticles. The dendrimers associated with these particles not only act to passivate and protect the particles, but can also provide a useful 'handle' with which to manipulate the particles and regulate their 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 nanoparticles; they are relevant for our understanding of the behavior of luminescent semiconductor nanoparticles as well.

### Q6.39

**FUNCTIONALIZED OCTAPHENYLSILSESQUIOXANES AS PRECURSORS TO NANOCOMPOSITE MATERIALS.** C. Brick, R.M. Laine, R. Tamaki, J. Choi, S-G. Kim, N. Takamura, K. Park,

Departments of MS&E, Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI.

**Introduction:** Functionalized octaphenylsilsesquioxanes  $[(\text{C}_6\text{H}_5\text{SiO}_{1.5})_8$ , 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 octaphenyl-silsesquioxane, 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:**

1. R.M. Laine, J. Choi, I. Lee, "Organic-Inorganic Nanocomposites with Completely Defined Interfacial Interactions," *Adv. Mater.* 13, 800-3 (2001).
2. J. Choi, J. Harcup, A.F. Yee, Q. Zhu, R.M. Laine, "Organic/Inorganic hybrid composites from cubic silsesquioxanes," *J. Am. Chem. Soc. ASAP Article* 10.1021/ja0107201S0002-7863 (01)00720-X.

### Q6.40

**NANOMETER-SCALE ORGANIC/INORGANIC MULTI-COMPOSITES IN SOLUTION IN THIN SOLID FILMS.** D.D. Richardson, S.R. Ely, M.J. McMurdo, P.G. Van Patten, Ohio University, Dept of Chemistry and Biochemistry, Athens, OH.

We have used functionalized poly(amidoamine) (PAMAM) dendrimers simultaneously to enclose CdS 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 ion. This allows us to very easily combine favorable excitation characteristics of the QD's with beneficial luminescence properties of the rare-earth ions. Because each nanoparticle is closely coupled to multiple acceptor ions, the QD's 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-, cathodo-, and electroluminescence measurements on thin films constructed from these new multicomposites will be presented and discussed in relation to the photophysical properties of these systems.

### Q6.41

**PERMSELECTIVITY OF HYBRID ORGANIC-INORGANIC POLYIMIDE COMPOSITES.** Chris J. Cornelius, Catalysis and Chemical Technologies Sandia National Laboratories Albuquerque, NM.

The permselectivity of a series of polyimide composites were evaluated utilizing He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, and CH<sub>3</sub>OH. Potential applications for these materials include membranes for direct methanol and hydrogen fuel cells, ion-exchange membranes, 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 synergistic properties exhibited by these materials. Physical property changes were reflected in changes in tan delta, glass transition temperature, thermal stability, and permselectivity changes.

### Q6.42

**EFFECT OF pH ON GELATION OF POLYSILSESQUIOXANES.** Duane A. Schneider, Colleen Baugher, Douglas A. Loy, Catalysts and Chemical Technologies 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(trialkoxysilyl)alkanes. While similar studies have been performed with tetraalkoxysilanes, silsesquioxanes have not been examined because few organo-trialkoxysilanes form gels. Those that do, fail to gel at the concentrations needed for accurate pH measurements. We were able to circumvent this problem by using bridged polysilsesquioxane that are known to readily form gels at concentrations low enough to allow accurate pH determinations.

### Q6.43

**THE STRUCTURAL DEFORMATION AND MECHANICAL PROPERTIES OF PERIODIC MESOPOROUS SILICA AND**

ORGANOSILICAS. Benjamin Hatton, D.D. Perovic, University of Toronto, Dept of MS&E; G.A. Ozin, University of Toronto, Department of Chemistry, Toronto, CANADA.

Self-assembled supramolecular arrays can act as templates for the sol-gel synthesis of inorganics to produce a variety of complex, 3-D nanostructures such as hexagonal 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 organic/inorganic nanocomposite [3], with mechanical properties that might mimic natural composites such as nacre. In addition, periodic mesoporous organosilica (PMO) materials have been developed recently to include a wide range of bridging organic groups (such as methylene, ethene, benzene) of the form  $O_3Si-R-SiO_3$  incorporated into the channel walls [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 will be presented. Nanoindentation 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 at 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.

- [1] S. Mann, G.A. Ozin. (1996) *Nature*, 382 (25 July), 313-318.
- [2] Kresge et al (1992). *Nature*, 359 (22 Oct), 710-712.
- [3] Johnson et al (1998) *J. Mater. Chem.*, 8(1), 13-14.
- [4] Asefa et al (1999). *Nature*, 402 (23/30 Dec), 867-871.
- [5] Gibson, Ashby (1997) *Cellular Solids*, 2nd Ed. Cambridge University Press.

#### Q6.44

SYNTHESIS AND CHARACTERIZATION OF POSS BASED OILS AS LUBRICANTS. Justin T. Leland, ERC Inc., Edwards Air Force Base, CA; Rusty Blanski, Brent Viers, AFRL/PRSM, Edwards Air Force Base, CA.

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 hydrosilation of long chain alpha-olefins with POSS hydrides proceeds with virtually quantitative yield. The synthesis and characterization of these materials, as well as thermal and viscosity data will be discussed.

#### Q6.45

ORGANIC/INORGANIC NANOCOMPOSITES FROM CUBIC SILSESQUIOXANES. Jiwon Choi, Ryo Tamaki, Chad Brick, Seunggyoo Kim, Albert F. Yee and Richard M. Laine, Departments of MS&E, Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI; Institute of Materials Research & Engineering, SINGAPORE.

Octasilsesquioxanes  $[(RSiO_{1.5})_8, \text{cubes}]$  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, aminophenyl, acetyl, have been successfully appended to these cubes and new hybrid composites have been prepared from them. Selected nanocomposites show excellent thermal/mechanical stabilities. Other composites offer well-defined nanostructure and nanoporosity of potential utility for applications ranging from electronics packaging materials to preconcentrators for MEMS gas chromatographic analysis. We present here our latest effort to expand the library of the functionalized cubes and to develop hybrid nanocomposites.

#### Q6.46

SYNTHESIS AND CHARACTERIZATION OF NOVEL HIGH MOLECULAR WEIGHT SILSESQUIOXANES. Kamyar Rahimian, Douglas A. Loy, David R. Wheeler, Sandia National Laboratories, Albuquerque, NM.

Trialkoxysilyl-containing monomers of the type  $(RO)_3Si(CH_2)_3C(O)OtBu$  (R = Me, Et) were prepared by hydrosilation of the

corresponding vinylic tert-butyl esters  $CH_3CHCH_2C(O)OtBu$ . 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 alkoxy groups while the tert-butyl ester functionality remains fully intact. Partial or full deprotection of the tert-butyl group can easily be achieved to yield the corresponding carboxylic 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 resins.

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#### Q6.47

Abstract Withdrawn.

#### Q6.48

CHARACTERIZATION OF  $Ti_6O_4(O_2CH_3)_8(OCH_2CH_3)_8$  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 tetraethoxide in the presence of methacrylic acid was characterized by electrospray - time of flight mass spectrometry (ESMS-TOF). The cluster has an approximately  $3 \times 7$  nm titanium oxide core. Clusters of this type are important as potential building blocks for organic-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 are useful in MS characterization of more complex chemical systems such as reaction mixtures of glass, ceramic, or hybrid material synthesis. The chemistry of such systems is not well known and ESMS is a powerful technique for studying the reactions of clusters in solution. While ESMS has been applied to the study of titanium alkoxide hydrolysis processes, mass spectra of isolated individual titanium oxide clusters have not previously been reported.

#### Q6.49

OPTICAL PROPERTIES OF CdSe NANOPARTICLE DOPED SOL-GELS. 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 nanocrystals are being imbedded in silica based sol-gels using 3-aminopropyltrimethoxysilane (APS) as a precursor. Semiconductor nanoparticles 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 been shown to enhance their stability towards decomposition. Moreover, sol-gels provide a porous structure (pores on the order of 3nm in our materials) that can allow the diffusion of small molecules to the imbedded chromophores. 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 nanoparticles, and the influence of surface sensitivity to small molecules including nitric oxide.

#### Q6.50

SYNTHESIS AND CHARACTERIZATION OF HOLLOW SPHERES INCORPORATED WITH MAGNETIC NANOPARTICLES. S.M. Saifur 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 many attentions in recent years. Assembly of polyelectrolytes on micron-sized polymeric spheres becomes an important subject because of various applications of sphere-based technologies. Layer-by-layer assembly is a straightforward approach that can be readily applicable for making functional structures. Our primary interests focus on the magnetically sensitive systems. We will report our work on the synthesis of hollow polymeric microspheres incorporated with magnetic nanoparticles such as ferrite ( $Fe_3O_4$ ) and FePt sandwiched in polyelectrolyte. We have also synthesized magnetic nanoparticle-bilayer composites. The structures of hybrid magnetic hollow spheres made by layer-by-layer assembly and those made by bilayer encapsulation have been examined using DSC, AFM, SNOM and TEM. The stability of these hollow spheres under the magnetic fields has been analyzed using optical microscope and fluorescence confocal microscope.

#### Q6.51

TIN TELLURIDE BASED INORGANIC/ORGANIC COMPOSITE

## MATERIALS WITH NANOSCALE PERIODICITY.

Andrew E. Riley, Sarah H. Tolbert, University of California, Los Angeles, Los Angeles, CA.

A combination of solution and solid phase chemistry has been used to synthesize new non-oxide based surfactant/inorganic composites with nanoscale periodicity. These composites are based on a tin telluride 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 tin telluride clusters, synthesized in the solid state, co-assemble with the quaternary ammonium surfactants in formamide solution. Oligomerization of the clusters appears to lead to favorable charge density matching 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 reorganization 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 tri-butyl phosphine to yield the final composite material. These results demonstrate that the concepts of solution phase inorganic/organic co-assembly can be extended from sol-gel type oxides to non-oxide materials.

### Q6.52

STUDY HYBRIDS ORGANIC AND INORGANIC PMMA, PMMA/HEMA CONTAINING DYES Tran Kim Anh, Pham Thi Minh Chau, Nguyen Trong Oanh, Tran Thu Huong, Nguyen Vu, Le Quoc Minh, Inst of Matis Sci, Natl Ctr for Natural Sci and Tech of Vietnam, Nghia 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 tetraethoxysilan (TEOS), in which blended different polymers. The dyes are Rhodamin 6G (Rh590), 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 Raman scattering, IR absorption, fluorescence, photoluminescent excitation spectra and lifetime.

### Q6.53

PYRENE FLUORESCENCE AS A MOLECULAR PROBE OF MISCIBILITY IN ORGANIC/INORGANIC HYBRID NANOCOMPOSITES SUITABLE FOR MICROELECTRONIC APPLICATIONS. Q.R. Huang, Curtis W. Frank, Dept. of Chemical Engineering, Stanford, CA; David Mecerreyes, James L. Hedrick, Willi Volksen, Robert D. Miller, IBM Almaden Research Center, San Jose, CA.

Fluorescence spectroscopy has been used to study the miscibility of MSSQ/P(MMA-co-DMAEMA) hybrid nanocomposites, which are useful in fabricating the new generation of spin-on ultra-low dielectric constant materials in the microelectronic industries. In this work, we have attached the pyrene group into the PMMA side chains. MSSQ with different amount of initial -SiOH (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 MSSQ 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 ratios also increase, suggesting that the MSSQ/P(MMA-co-DMAEMA) hybrid nanocomposites move toward greater immiscibility. The fluorescence results also show that, the lower the amount of initial silanol groups in MSSQ, 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 MSSQs studied.

### Q6.54

GAS ADSORPTION STUDIES OF AMINO-FUNCTIONAL INORGANIC-ORGANIC HYBRID MATERIALS. Noriko Yamada, Takao Kanai, Yuji Kubo, Keiko Kawakami and Takeshi Hamada, Advanced Technology Research Laboratories, 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 aminopropyl groups (AP), dimethylaminopropyl groups (DMAP) and diethylaminopropyl groups (DEAP) were prepared from organotrialkoxysilane with each amino groups and tetraethoxysilane (TEOS) in a molar ratio of 0.25: 0.75. Amino-functional hybrid powders were exposed to NO, NO<sub>2</sub> and SO<sub>2</sub> as a 0.5% mixture in argon. Reactions of the acidic gases with AP, DMAP 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 NO<sub>2</sub> was larger than that of SO<sub>2</sub> in all the amino-functional hybrid powders. The selectivity (the adsorption amount of NO<sub>2</sub> / that of SO<sub>2</sub>) and the sorption capacity were found to be affected by the kind of amino groups. DMAP-functional hybrid showed the largest sorption capacity to both NO<sub>2</sub> and SO<sub>2</sub>. Research supported by NEDO, under the Synergy Ceramics Project promoted by METI, Japan.

### Q6.55

HYBRID ORGANIC-INORGANIC MATERIALS DESIGNED TO CLEAN WASH WATER IN PHOTOGRAPHIC PROCESSING: GENESIS OF A SOL-GEL INDUSTRIAL PRODUCT: THE KODAK WATER SAVING TREATMENT SYSTEM. Jean Guilment, Didier Martin, Olivier Poncelet, Kodak Industrie Research Lab, Chalon Sur Saone, FRANCE.

Environmental laws concerning the water become more and more stringent year after year in European Union (AT2950 in France, Legge Merli in Italy). The classical silver halide photoprocessing requires at least 3 steps which are the developing, the fixing and the washing. The washing step uses a large amount of water which is discarded in the sew. In July 2000 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 1mg/l. The Kodak Water Saving Treatment System has been designed to help our customers to be in compliance with the Law. This system has two functions, the release of biocides cocktails and the trapping of silver. Two aluminosilicate gels (imogolite-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 which is a hybrid organic-inorganic composite (imogolite modified by controlled hydrolysis of thio organo silicium alkoxides) allows to trap silver. These gels are extremely robust versus time and chemicals (pH). This paper will describe the synthetic way, their characterization (Raman) and the obtained performances in various configurations after one year on the market. Others 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. Zhongcai 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 micronmeter. Two-types of polymer microspheres used are poly(methyl methacrylate-*c*-styrene) and poly(acrylonitrile-*c*-styrene) networks respectively. We have observed that the glass transition ranges of the polymer matrices 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 micronmeter, which suggests that the metallic coating can facilitate quick establishment of a uniform temperature field within the polymer beads that has a diameter below 100 micronmeter. 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 metallic cloth. It is anticipated that those 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 BACTERICIDAL ANTI-FOULING. Sung Ho Kim, Seung-Yeop Kwak, 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 underneath the titanium dioxide

(TiO<sub>2</sub>) nanosized particles have been fabricated by a molecular self-assembly process, aiming at breakthrough of biofouling problems. First, positively charged particles of the colloidal TiO<sub>2</sub> sol was synthesized by a sol-gel process and the size of the resulting particles in acidic aqueous solution was estimated to be  $d \approx 2$  nm by analyzing the UV-visible absorption characteristics with a quantum mechanical model developed by Brus. Transmission electron microscopy (TEM) further confirmed the formation of the quantum-sized TiO<sub>2</sub> particles ( $\sim 10$  nm or less). The TiO<sub>2</sub> particles appeared to exist in the crystallographic form of anatase as observed with the X-ray diffraction (XRD) pattern in comparison with those of commercial 100 % rutile and commercial 70:30% anatase-to-rutile mixture. The hybrid thin-film-composite (TFC) aromatic polyamide membranes were prepared by self-assembly of the TiO<sub>2</sub> nanoparticles on the polymer chains with COOH groups along the surface. They showed improved RO performance in which the water flux even increased, though slightly. Field-emission scanning electron microscopy (FE-SEM) exhibited the TiO<sub>2</sub> nanoparticles well adsorbed onto the surface. X-ray photoelectron spectroscopy (XPS) demonstrated quantitatively that a considerable amount of the adsorbed particles were tightly self-assembled at the expense of the initial loss of the loosely bound and became stabilized even after exposure to the various washing and harsh RO operating conditions. The antibacterial fouling potential of the TiO<sub>2</sub> hybrid membrane was examined and verified by measuring the viable numbers and determining the survival ratios of the *Escherichia coli* (*E. coli*) as a model bacterium with and without UV light illumination. The photocatalytic bactericidal efficiency was remarkably higher for the TiO<sub>2</sub> hybrid membrane under UV illumination, compared to that of the same membrane in darkness, as well as those for the neat membranes in darkness and with UV illumination.

SESSION Q7: TEMPLATED GROWTH TO NANO/MESO/MACRO-STRUCTURED HYBRIDS MATERIALS I

Chairs: Clement Sanchez, C. Jeffrey Brinker and Thomas Bein

Wednesday Morning, April 3, 2002  
Metropolitan II (Argent)

8:30 AM \*Q7.1

ORGANIC-CONTAINING MESOPOROUS SILICAS WITH A VARIETY OF MESOPHASES AND A PERIODIC PORE WALL STRUCTURE. Shinji Inagaki, Toyota Central R&D Labs., Inc., Aichi, JAPAN.

Since the discovery of ordered mesoporous silicates M41S and FSM-16 in 1992-93, a variety of ordered mesoporous materials have been synthesized by a template method, using supramolecular assembly of surfactant molecules. Mesoporous materials now include a variety of inorganic materials, e.g., non-Si transition-metal oxides, phosphates, metallic platinum and carbon. On the other hand, many kinds of sol-gel derived organic-inorganic hybrid amorphous materials have been synthesized, in which new catalytic and adsorption functions can be used in the stable inorganic matrix. Although these amorphous materials have a homogeneous distribution of organic groups and inorganic oxide, they have disordered structures and scattered pore-size distributions. We recently reported the synthesis of organic-inorganic hybrid mesoporous materials with an organic-bridging structure in the silica network and regularly arranged pores with uniform size of ca. 3nm. The organic-bridged mesoporous materials are synthesized by condensation of organosilane molecules possessing two silyl groups [-Si(OR)<sub>2</sub>]<sub>2</sub> bridged with various organic groups (R1), (R<sub>2</sub>O)<sub>3</sub>Si-R1-Si(OR)<sub>2</sub>, in a surfactant solution. Ethane (-CH<sub>2</sub>CH<sub>2</sub>-) bridged mesoporous material formed a variety of mesophases with highly ordered 2D-hexagonal (one-dimensional channel), 3D-hexagonal (3D-cage) and cubic Pm-3n (3D-cage) symmetries. They showed well-defined rod-like particles with a hexagonal cross-section (2D-hexagonal), spherical particle (3D-hexagonal) and decaoctahedral (18-hedral) particle (cubic Pm-3n). The flexible and the appropriate length of the C<sub>2</sub> hydrocarbon chain enable us to form a variety of highly ordered mesoporous materials. Benzene (-C<sub>6</sub>H<sub>4</sub>-) bridged mesoporous material formed a unique nano- and Ångström-scale hierarchically ordered structure. The material has not only a 2D-hexagonal mesostructure with a lattice constant of 52.5 Å but also a layered structure with a basal spacing of 7.6 Å in the pore walls. The layered structure in the walls was formed by self-assembly of benzene-bridged organosilane molecules due to the hydrophobic and hydrophilic interaction. This is the first example of mesoporous material possessing a crystal-like ordered pore-wall structure.

9:00 AM \*Q7.2

SELF-ORGANIZED HYBRID SOLIDS. Joel J.E. Moreau,

Hétérochimie Moléculaire et Macromoléculaire, Ecole Nationale Supérieure de Chimie, Montpellier, FRANCE.

Sol-gel chemistry allowed the synthesis of organo-poly-silsesquioxanes having a well defined three-dimensional network owing to the presence of covalent bonds between organic and inorganic fragments. A step beyond the synthesis of new hybrid materials, with unique properties resulting from mixing organic and inorganic at the molecular level, consists in the controlled synthesis of organized materials. The creation of hybrids with well-ordered mesopore structure was recently obtained by use of external organic surfactant templates as it was first reported in the synthesis of silica mesophases. The combination of organic and inorganic substructures in silsesquioxane hybrids offers unique possibilities for designing new synthetic routes. Hybrids have large potentialities since the organic component can itself exhibit diverse self-assembly properties and may direct the formation of the three-dimensional hybrid network in a self-organization process. We studied the use of supra-molecular interactions, based on the association properties of urea groups by H-bond or on the hydrophobic properties of long hydrocarbon chains, between precursor molecules during the hydrolysis and condensation of (RO)<sub>3</sub>Si-R'-Si(OR)<sub>3</sub>. A bis-silylated molecule capable of auto-association gave rise to self-organized hybrid silica with a medium long range ordered lamellar structure. The inter-layer spacing varied according to the length of the organic spacers in the precursor. Evidence for a control of the solid morphology was also shown in the hydrolysis of chiral units, capable of association by H-bond. It allowed the creation of right and left-handed helical hybrid silica fibers, according to the (R,R) or (S,S) configuration of the chiral organic unit. The self-assembly properties which can be assigned to the organic units, offer possibilities for achieving a structure control at different scales.

9:30 AM Q7.3

CONTROLLED DESIGN OF MESOSTRUCTURED TITANIA BASED MATERIALS. Galo J. de A.A. Soler-Illia, David Grosso, Eduardo L. Crepaldi, Florence Cagnol and Clément Sanchez, Chimie de la Matière Condensée, UPMC - CNRS, Paris, FRANCE.

Mesostructured hybrid 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 tuning the hydrolysis-condensation of the metallic cations with the self-assembly of the organic counterparts. While much progress has been attained in silica-based materials, interest and positive results in transition metal (TM) oxide-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 TiO<sub>2</sub>-surfactant hybrid xerogels and thin films, presenting hexagonal mesostructure (p6m) are obtained from ethanol/HCl/H<sub>2</sub>O media, after selective solvent evaporation. The formation kinetics of the mesophase is followed by SAXS, interferometry 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. Organized Titanium oxide-hybrid structures are reproducibly formed through cooperative self-assembly between hydrophilic Ti-oxo nanometric building blocks and the micellar template. The hydrophilic matching approach proposed in this work has been extended to other titania systems, using both ionic or nonionic 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 titania based hybrids leads to high surface (350-400m<sup>2</sup> g<sup>-1</sup>) phosphorus-free mesoporous titania; the mesostructure is retained at a temperature as high as 350°C. This approach can be successfully extended to other nonsilicate based meso-structured materials.

9:45 AM Q7.4

INORGANIC-ORGANIC HYBRID SURFACTANTS IN THE SYNTHESIS OF MESOSTRUCTURED SILICA. Nicola Huesing, Beatrice Launay, Josef Bauer, Guido Kickelbick, Vienna University of Technology, Inst of Inorganic Chemistry, Vienna, AUSTRIA.

Well-defined amphiphilic block copolymers containing a poly(dimethyl siloxane) (PDMS) and a poly(ethylene oxide) block (PEO) were synthesized by anionic ring-opening polymerization of hexamethylcyclotrisiloxane, followed by chain extension with a PEO block of a defined length. These amphiphilic molecules were used as templates in a solvent evaporation-driven synthesis approach to self-assembled mesostructured silica films. The structural properties of the film depend to a high degree on the size and ratio of the different blocks in the template molecule. X-ray diffraction, transmission electron microscopy, and 29Si and 13C solid state NMR were used to

characterize the final film. The inorganic-organic copolymer template offers the interesting possibility to convert parts of the template molecule into silica, and therefore, to modify, reinforce and thicken 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 PDMS block completely decomposes only above 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 HYBRID COLLOIDS BY SUSPENSION POLYCONDENSATION USING HYDROPHILIC BLOCK COPOLYMERS. Corine Gerardin, Nicolas Sanson, Francesco Di Renzo, Francois Fajula, CNRS-Ecole Nationale Supérieure de Chimie, Montpellier, FRANCE; Olivier Anthony, CNRS Rhodia 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 hydroxides were obtained by forced hydrolysis of metal ions in presence of water-soluble diblock copolymers. The block copolymers contain one metal-complexing polyelectrolyte 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 as the complexing functions act as poisons of the 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 steps were characterized. The synthesis route implies, first, a step of induced micellization of the hydrophilic copolymers. It is due to complexation of the mineral precursors by the polyacrylate blocks leading to insoluble complexes. Organic-inorganic micelle-like assemblies are thus formed, which present a core-shell 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 hairy 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 HYBRID MULTIFUNCTIONAL MESOPOROUS MATERIALS: SUBSTITUTION OF OXIDE AND ORGANIC MOIETIES OF PERIODIC MESOPOROUS ORGANOSILIC MATERIALS BY HETEROATOM FUNCTIONAL GROUPS. Tewodros Asefa, Neil Coombs, Hiltrud Grondy, Mark J. MacLachlan, Geoffrey A. Ozin, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA; Mietek Jaroniec, Michal Kruk, 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 organic-inorganic hybrid materials. We recently developed various synthetic routes to a new class of hybrid materials called periodic mesoporous organosilicas (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 heteroatom functional groups forming new types of multifunctional nanocomposites that are otherwise impossible or difficult to prepare by other methods. These novel materials may find applications in catalysis and separations, 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. Schroden, Mohammed Al-Daous, Hongwei Yan, 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 a few hundred nanometers in diameter. 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 after formation of the porous support by grafting processes. This talk will focus on surface functionalization of macroporous 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(M=Al,B) IMIDES VIA A NON-AQUEOUS SOL-GEL ROUTE. Fei Cheng, Berangere Toury, Ralf Supplit, 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 diimide  $\text{Si}(\text{NH})_2$  gels (precursors to high purity  $\text{Si}_3\text{N}_4$ ) by acid catalyzed ammonolysis of tris(dimethylamino)silylamine  $(\text{Me}_2\text{N})_3\text{SiNH}_2$ .<sup>1</sup> In this work, we report the preparation of mesoporous multinary Si-M (M=Al, B) imidosilicates via ammonolytic sol-gel processing of new single source precursors. The precursor moleculars tris[(dimethylamino)silylamino](tetrahydrofuran)alanane  $(\text{C}_4\text{H}_8\text{O})\text{Al}[\text{NHSi}(\text{NM}_2)_3]_3$ , **1**, and 2,4,6-tris[tri(dimethylamino)silylamino]borazine  $[(\text{Me}_2\text{N})_3\text{SiNH}]_3\text{B}_3\text{N}_3\text{H}_3$ , **2**, were prepared from the lithium salt of  $(\text{Me}_2\text{N})_3\text{SiNH}_2$  and aluminium trichloride or trichloroborazine respectively. A translucent semi-rigid Si-Al imide gel, **3**, and an analogous Si-B imide gel, **4**, were prepared by acid catalyzed ammonolysis 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 solids. The IR spectra of both gels showed broad  $\nu(\text{N-H})$  bands at 3200-3550  $\text{cm}^{-1}$ , suggesting the presence of NH groups with different environments. Bands at 735  $\text{cm}^{-1}$  in the IR spectrum of gel **3** and 1479  $\text{cm}^{-1}$  in the spectrum of gel **4** can be ascribed to Al-N and B-N bonds respectively. Both gels showed  $\nu(\text{Si-N})$  and  $\delta(\text{N-C})$  at 1190 and 920  $\text{cm}^{-1}$  respectively. The low intensity of  $\nu(\text{CH})$  bands from 2796 to 2993  $\text{cm}^{-1}$  for both gels indicated the presence of detectable amount of residual dimethylamino groups. These spectral features identified the gels as silicon aluminum and silicon boron imides, containing residual dimethylamino groups:  $\text{SiM}(\text{NH})_x(\text{NH}_2)_y(\text{NM}_2)_z$  (M=Al, B). TG-MS analysis of the gels showed that dimethylamine and ammonia were evolved below 700°C, consistent with the IR results. Both gels exhibited mesoporous structures and had total surface areas of 528  $\text{m}^2/\text{g}$  for **3** and 692  $\text{m}^2/\text{g}$  for gel **4**.

<sup>1</sup> R. Rovai, C.W. Lehmann and J.S. Bradley, *Angew. Chem. Int. Ed.*, **38**, 2036 (1999).

#### 11:45 AM Q7.9

Abstract Withdrawn.

### SESSION Q8: TEMPLATED GROWTH TO NANO/MESO/MACRO-STRUCTURED HYBRIDS MATERIALS II

Wednesday Afternoon, April 3, 2002  
Metropolitan II (Argent)

#### 1:30 PM \*Q8.1

BLOCK COPOLYMER - INORGANIC HYBRID MATERIALS FROM ORGANICALLY MODIFIED CERAMIC PRECURSORS. Uli Wiesner, Cornell Univ, Dept of MS&E, 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 polymers as well as ceramic 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. The potential for new functional materials lies in the versatility of the polymer chemistry as well as that of the sol-gel 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 nanobiotechnology. 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.



**2:00 PM \*Q8.2**

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-weight 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 physicochemical processes involved are generally complicated, because of the heterogeneous, multicomponent, and non-equilibrium natures of these systems. In particular, interactions at 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.

**2:30 PM Q8.3**

PERIODIC MESOPOROUS ORGANOSILICAS WITH DIFFERENT ORGANIC BRIDGING LIGANDS - SYNTHESIS AND CHARACTERIZATION. Vivian Rebbin, Michael Froeba, 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 M41S silica materials [1]. For the first time bridged silsesquioxane precursors, e.g. 1,2-bis(trimethoxysilyl)ethane, were used as silica 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 1000 m<sup>2</sup>/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.

[1] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 1999, 121, 9611.

[2] O. Muth, C. Schellbach, M. Froeba, Chem. Commun. 2001, 19, 2032.

**2:45 PM Q8.4**

SYNTHESIS AND CHARACTERIZATION OF MESOSCOPICALLY ORDERED SURFACTANT/Co-SURFACTANT TEMPLATED METAL OXIDES. Mika Linden, Teresa Czurylskiewicz, 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 substituted, aromatic swelling agents with or without the use of non-ionic co-surfactants 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 mesostructures could controllably be increased up to 80 Å (TMB/CTAB molar ratio = 4) without the loss of the long-range order of the hexagonal mesophase. Increasing the TMB content further lead to a transition to a lamellar phase through a hexagonal-lamellar co-existence region. TMB was much more efficient than toluene in swelling the mesostructure, 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 1-octanol as a co-surfactant, the octanol/TMB 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. However, loss of order for both titania and zirconia was usually observed upon removal of the template. On the

contrary, the d-spacing of SBA-3 type 2-D hexagonally ordered silica could controllably be increased using the same approach, clearly indicating the potential of the use of mixed surfactant templates together with a swelling agent for the synthesis of large pore mesoscopic materials.

**3:15 PM \*Q8.5**

SELF-ASSEMBLY AND TEMPLATING STRATEGIES FOR HYBRID MATERIALS. Samuel I. Stupp, Department of MS&E, Department of Chemistry, and Medical School, Northwestern University, Evanston, IL.

Organic-inorganic hybrid materials designed at the nanoscale to have specific functions are still in very early stages of development. In conventional composites inorganic microphases are mechanically dispersed in organic matrices with varying degrees of interfacial adhesion, and these materials yield structures with high strength to density ratios. In order to integrate increasingly sophisticated functionalities in hybrid materials that can be synthesized at low temperature, design at the nanoscale and the use of self-assembly become attractive strategies. Another useful strategy is "biomimetics" given that biology has been exceedingly successful in designing remarkable hybrids through evolution. The bone family ranks at the very top of the scale in complexity and sophistication. In this lecture self-assembly and templating are discussed as strategies to create hybrids in which both inorganic and organic components are nanophases that can interact strongly with each other through noncovalent interactions. One of the examples to be discussed is the self assembly of peptide nanofibers in water with the capacity to nucleate and organize hydroxyapatite crystals in a fashion that recreates the nanostructure of bone. In another example metal oxide nanocrystals are aligned by self assembling organic nanoribbons and weak electric fields to produce effective ultraviolet lasing materials. A third example to be discussed is the templating of II-VI semi-conductors by the same nanoribbons resulting in hybrid objects that might be useful in nanotechnology.

**3:45 PM \*Q8.6**

SYNTHESIS OF ORDERED MESOPOROUS CARBONS BY NANOCASTING WITH SILICA TEMPLATES. Sang Hoon Joo, Hyun June Shin, Tae Wan Kim, Ryong Ryoo, Korea Advanced Institute of Science and Technology, Department of Chemistry, Taejon, KOREA.

Mesoporous carbons attract much attention in modern science and technology, including purification, separation, catalysis, electrochemical applications and energy storage. Here, we present our recent works on the synthesis of the ordered mesoporous carbons designated as CMK-n. These mesoporous carbons are synthesized by the nanocasting procedure which consists of the infiltration of organic compounds into mesoporous silicas, carbonization to form mesoscopically ordered carbon-silica composites and subsequent removal of the silica frameworks. The mesoporous carbons are obtained with uniform pore diameters, tunable typically in the range of 2 ~ 6 nm, with high specific BET surface areas, various pore shapes and connectivity, depending on structures of the templates. The ordered mesoporous carbons suggest many new research possibilities, whereas disordered porous carbons are irregularly structured on the long-range scale so that the structural properties are difficult to characterize with ordinary X-ray powder diffraction (XRD). The presence of the distinct XRD patterns provides new opportunities for precisely monitoring various physicochemical phenomena taking place inside the well-defined carbon pores or at the pore walls such as adsorption, impregnation, framework changes, formation of metal clusters and grafted functional groups, using an ordinary powder XRD technique. The carbons constructed with such well defined and controllable pore diameters may be used as standard materials for the characterization of the carbon porosity. The carbon materials are suitable as a new hydrophobic support for catalytic components that are more suitable for organic reactions compared with mesoporous silicas. Extremely high metal dispersion of Pt, Pd and Ru can be achieved when supported on these new types of carbon materials. The high metal dispersion is in high demand as a means of improving traditional platinum catalysts and also to meet the high-current output required in advanced fuel cells systems. The carbon frameworks can also be grafted with various organic functional groups.

SESSION Q9: ADVANCED PROCESSING FOR  
HYBRID MATERIALS

Chairs: Kenneth J. Balkus and Christophe J.A. Barbe  
Thursday Morning, April 4, 2002  
Metropolitan II (Argent)

**8:00 AM \*Q9.1**

MICROSTRUCTURAL EVOLUTION WITH TEMPERATURE OF

MESOPOROUS SILICA FILMS STUDIED BY FTIR SPECTROSCOPY. Plinio Innocenzi, Paolo Falcaro, Dipartimento di Ingegneria Meccanica, Settore Materiali, Universite di Padova, Padova, ITALY; David Grosso, Chimie de la Matiere Condensee, Universite Paris 6, Paris, FRANCE.

Silica mesoporous thin films have been synthesised with a self-assembling process employing cetyltrimethylammonium bromide as the organic template and tetraethyl orthosilicate as the silica source. Mesoporous films with 3D-Hexagonal and 3D-Cubic phases have been obtained with different protocol of synthesis after silicon substrates have been dip-coated in the precursor solution in controlled humidity conditions. The films have been thermally treated in air with a progressive heating schedule from as-deposited up to 1000°C. The evolution of the microstructure has been studied with transmission Fourier transformed 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<sup>-1</sup>, whose intensity gradually decreased with the thermal treatment. At temperatures larger than 350°C cyclic species have been no more observed. In the 1000-1300 cm<sup>-1</sup> region several overlapped absorption bands have been detected. In particular, we have resolved the pair LO<sub>3</sub>-TO<sub>3</sub>, the cyclic species absorption band and the pair LO<sub>4</sub>-TO<sub>4</sub>. These last bands, in particular are associated with order-disorder transitions that is the microstructural evolution that we deduce to happen 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 1000-1300cm<sup>-1</sup> region has been better understood with the Berreman configuration, performing the transmission FTIR analysis at 45° with respect to the normal incidence angle. The LO<sub>3</sub> 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. At temperatures larger than 500°C the LO<sub>4</sub>-TO<sub>4</sub> pair is almost completely disappeared, in accordance to another order-disorder transition of the silica microstructure. The TO<sub>3</sub> 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

DAM-1 MOLECULAR SIEVE FORMS, FIBERS AND FILMS. Kenneth J. Balkus, Jr., Decio Coutinho, Suhda Madhugiri, Claudia Meek, Paul Pantano, 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 nanoporous materials. The required form of a molecular sieve may involve dramatically different length scales, ranging from shape particles to fibers to continuous coatings. Our efforts in this area will be illustrated using various examples of these forms based on Dallas Amorphous Materials one (DAM-1). This mesoporous molecular sieve was synthesized using water soluble Vitamin E TPGS as the template. In addition to potential drug delivery applications for this inorganic/organic composite, the hierarchical forms DAM-1 may be employed in areas ranging from catalysis to sensors. The morphogenesis of DAM-1 shaped particles as well as applications in molecular recognition and optical sensing will be described. We have also developed a novel process for spinning DAM-1 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 DAM-1 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 vapour deposition (CVD) at low pressures and room temperature. The oxides form on the surface of the substrate (template) by reacting silane and silane/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 oxide 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 electrospun 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 ORGANOSILICA SOL-GEL SURFACES. Bakul C. Dave, Mukti S. Rao, Dept. of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL.

Sol-gel-derived silicates exhibit gradual yet reproducible variations in their physical state along the sol-gel-xerogel structural coordinate. 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 means of external templates as structure-directing agents such that 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 glass. This presentation will focus on recent results obtained in our lab for introducing 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. Barbe, B.A. Latella, M. Ignat, D.J. Cassidy, K.S. Finnie, J. Hanna and J.R. Bartlett, ANSTO, Mensai, 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 the substrate. 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 alkyl-trimethoxy silanes (MTMS, VTMS and GTMS). The integrity 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. Simultaneous, in-situ micromechanical 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 MESOPOROSITY OF TRIBLOCK COPOLYMER-TEMPLATED SILICA. CHARACTERISATION AND CONTROL. Francesco Di Renzo, Anne Galarneau, Helene Cambon and Francois Fajula, ENSCM, Catalytic Materials Laboratory, Montpellier, FRANCE.

Silica-triblock copolymer mesophases are effective precursors for ordered mesoporous oxides [1]. SBA-15, a hexagonal mesophase formed in the presence of EO20-PO70-EO20 surfactant, differs from MCM-41, a hexagonal mesophase formed in the presence of cationic surfactants, by its stability and adsorptive properties [2, 3]. In this communication, a model is presented for the pore system of SBA-15, allowing to evaluate the amount of micropores present in the silica walls between the main channels [4]. The rugosity of the mesopore surface 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 moiety in composite mesophases and the secondary connections inside the organic moiety.

1. D.Y. Zhao, Q.S. Huo, J.L. Feng, B.F. Chmelka and G.S. Stucky, J. Am. Chem. Soc., 1998, 120, 6024.
2. M. Impéror-Clerc, P. Davidson and A. Davidson, J. Am. Chem. Soc., 2000, 122, 11925.
3. P.I. Ravikovitch and A.V. Neimark, J. Phys. Chem. B, 2001, 105, 6817.
4. A. Galarneau, H. Cambon, F. Di Renzo and F. Fajula, Langmuir, in press.

#### 10:30 AM Q9.7

PHASE SEPARATION IN ALKYL-BRIDGED POLYSILSES-

QUIOXANE SOL-GEL SYSTEM. Kazuki Nakanishi, Takamitsu Yamato, Kazuyuki Hirao, Kyoto Univ, Dept of Material Chemistry, Graduate School of Engineering, Kyoto, JAPAN.

Phase separation and concurrent sol-gel transition behavior of polymerizing bis(trialkoxysilyl)alkanes has been investigated under acidic conditions. Concurrent spinodal decomposition and sol-gel transition of hydrolyzed bis(trimethoxysilyl)hexane resulted in well-defined co-continuous phase-separated structures. The phase separation tendency was found to be much lower than those in alkyltrialkoxysilane system. After removal of the solvent phase, sharply distributed macropores were obtained in the size range of 0.1 to 5  $\mu\text{m}$  and twig-like thin co-continuous gel domains were observed.

#### 10:45 AM Q9.8

EXPLORING THE ROLE OF NANOMETER SCALE ARCHITECTURE ON HIGH-PRESSURE DEFORMATIONS IN PERIODIC SILICA/SURFACTANT COMPOSITES.

Sarah H. Tolbert, Junjun Wu, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA.

In this presentation we explore the unique structural properties of periodic surfactant-templated silicas 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  $\sim 4$  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%), suggesting that 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 distortions are reversible upon release of pressure. 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 distorts 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

GAS PHASE DEPOSITION OF HYBRID COATINGS. G.R. Alcott, Dept. of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS; J.L. Linden, TNO-TPD, Eindhoven, THE NETHERLANDS; M.C.M. van de Sanden, Dept. of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS.

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  $\text{SiO}_2$  films with properties such as 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 namely, a reduction in process steps 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/ $\text{O}_2$  gas stream is injected into a high density plasma (1 kW maximum power) generating inorganic  $\text{SiO}_2$  active species which are incorporated into a growing plasma polymer film. Films are grown from the precursor TEOS, TMSE and TPS evaluated with respect to mechanical, chemical and optical properties, using scratch resistance (Taber abrasion), Methyl ethyl ketone (MEK), adhesion and visible transmission measurements. Structural and chemical properties are determined using IR spectroscopic measurements coupled with spectroscopic ellipsometry. The process chemistry and mechanisms are studied using in situ mass spectroscopy, in situ FTIR and spectroscopic ellipsometry.

#### 11:15 AM Q9.10

ELECTRIC FIELD INDUCED TEMPLATING METHODS FOR MESOPOROUS SEMICONDUCTING AND METALLIC FILMS. Kyoung-Shin Choi, Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA; Eric W. McFarland, Department of Chemical Engineering, University of California, Santa Barbara, CA; Galen D. Stucky, Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA.

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 ( $\sim 5$  wt%). An electric field applied during the deposition process can provide a very unique and extreme environment for charged particles in that the electrode-electrolyte interface exhibits a drastic potential gradient, creating remarkably high concentrations of charged species at the electrode interface. This unique condition can be exploited to electrodeposit mesostructured films by adding 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 layers of liquid crystalline phases. As a result, the mesostructures 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 our 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 electrocatalytic 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-GEL GLASSES : ADVANTAGE OF BICOMPONENT PHOTOACTIVE SYSTEMS. Olivier Soppera, C  line

Croutx  Barghorn, Christiane Carr  , Dept of Photochemistry, CNRS UMR 7525, Mulhouse, FRANCE.

Use of organosilanes as hybrid systems is of increasingly 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, characteristics of the organic part have to be adapted with the view of optimizing the properties of the final material. Hybrid materials used in this study consisted of organosilane precursor with methacrylate functions, titanium isopropoxide, methacrylic acid and photoinitiator. The polycondensation of the inorganic component was achieved sequentially and simultaneously with the photopolymerization of the organic one to provide a mutually interpenetrating network. Polymerization in the UV range presents the advantages of fast-curing at temperatures compatible with fragile substrates and spatio-temporal selectivity of the reaction. Characteristics of the photopolymerization process taking place in hybrid sol-gel materials were investigated by UV and Real Time FTIR spectroscopy. Besides the study of the organic network, NMR investigations led information relative to the inorganic network formation during the sol maturation. The whole results provide insights into the optimization of the photochemical step. Indeed, it was demonstrated that titanium components added as passive components to increase the refractive index of layer, can induce polymerization under a medium pressure mercury arc lamp irradiation. In addition, mix photoactive systems involving an organic photoinitiator and titanium components were investigated and led to a better efficiency of the photoinitiation. 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

Chairs: Kazuki Nakanishi and Jean-Francois Gerard  
Thursday Afternoon, April 4, 2002  
Metropolitan II (Argent)

#### 1:30 PM \*Q10.1

TOWARDS HIGH RESOLUTION 1H SOLID STATE NMR SPECTRA IN HYBRID MATERIALS. L. Camus, V. Goletto, C. Bonhomme, F. Babonneau, Chimie de la Mati  re Condens  e, UPMC, Paris, FRANCE.

A large class of hybrid materials for applications in the fields of protective coatings, optical devices, sensors, catalysts are 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 requires a good understanding of these 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 often suffer from a lack of resolution due to the large 1H-1H dipolar coupling that usually exists in these highly protonated systems. Commercial MAS-NMR probes are now available that can reach spinning rates up to 35 kHz, and thus can allow to record high resolution 1H MAS-NMR spectra, especially when combined with high magnetic field (14.1 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 molecules. In both cases, emphasis will be put on the characterisation of the spatial proximity between the host molecules and the matrix.

#### 2:00 PM \*Q10.2

TEMPLATING IN NANOPOROUS SILSEQUIOXANES: SOLID-STATE NMR STUDIES. Peter A. Mirau 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/propylene oxide triblock copolymers and methyl silsesquioxane. 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 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 silsesquioxane matrix. The results show that the domain size and the interfacial 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 NANOPARTICLES 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; Weiliang Gong, Werner Lutze, Catholic Univ of America, Vitreous State Laboratory, Washington, DC; C. Jeffrey Brinker, Univ of New Mexico, Center for Micro-Engineered Materials and Dept of Chemical and Nuclear Engineering, Sandia National Laboratories, Albuquerque, NM; John A. Shelnut, 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. Self-assembly of mesostructured silica thin films offers a potential means for incorporating such photocatalytic 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 exposure to visible light, 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 and nanowires 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 confined by the mesopore 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 silica mesopores templated by different surfactants. The success of this process offers a range of applications, from cleaning up heavy metal contaminated water to photolithographic growth of metal nanowires.

#### 2:45 PM Q10.4

SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF MIXED-PHASE MICROPOROUS-MESOPOROUS MATERIALS. Raja H.P.R. Poladi, Christopher Landry, Univ of Vermont, Cook Physical Science Bldg, Burlington, VT.

Mixed-phase microporous-mesoporous materials have been produced by a two-step synthetic process. These solids, called MMM-1 (MCM-41/MFI phases) and MMM-2 (MCM-48/MFI phases), have been characterized by X-ray diffraction (XRD), nitrogen physisorption, and electron microscopy. At early stages of crystallization at 170°C, mesoporous phases were formed exclusively, while at longer heating times MFI was formed. At intermediate times, MMM-x were formed with varying amounts of MFI depending on the crystallization time. XRD indicated that MMM-1 could be severely oriented by sample preparation, which was consistent with an unusual ribbon-like morphology observed in TEM. This morphology was not observed for either pure MCM-41 or MFI. Al-MMM-1 was also synthesized, and was used for the isomerization of xylene. These

experiments showed that Al-MMM-1 has a higher selectivity for p-xylene than either Al-MCM-41 or Al-MFI (ZSM-5). Finally, Ti-MMM-1 was synthesized and was used in the oxidation of alkanes. IR spectroscopy indicated that the mixed-phase material contained framework Ti species and has more atomic order within its walls than Ti-MCM-41. Ti-MMM-1 was shown to be more selective for alkane oxidation than either Ti-MCM-41 or Ti-MFI (TS-1).

#### 3:15 PM \*Q10.5

CHARACTERIZING POROSITY IN NANOPOROUS THIN FILMS USING POSITRONIUM ANNIHILATION LIFETIME SPECTROSCOPY. David Gidley, William Frieze, Department of Physics, University of Michigan, Ann Arbor, MI; Jianing Sun, Hu Yifan, Department of MS&E, 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 142 ns is reduced by collisions with the pore surfaces. The collisionally reduced Ps lifetime is correlated with pore size and is the key feature in transforming a Ps lifetime distribution into a pore size distribution. In hybrid films made porous by a degradable porogen PALS readily detects a percolation threshold in porogen loading that represents the transition from closed pores 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-Jacques Gaumet, LSMCL, Metz University, Metz, FRANCE; Geoffrey Strouse, 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. All these analytical tools are excellent for average 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 composition, size, surface and stability of nanoparticles. We have successfully applied mass spectrometry to the analysis of i) nano-scale semiconductor (Cd/Zn - S/Se) materials up to 3.0 nm and on ii) methacrylate-modified titanium alkoxide containing a Ti<sub>6</sub>O<sub>4</sub> core, which can be precursor of organic polymeric network in addition to an inorganic network, combining properties of inorganic and organic materials. By using ESI, specific fingerprints were found for 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 been also 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. Roy, B. Sahut, Protavic, Levallois, FRANCE; P. Gaucher, A. Jacobelli, Thales Research and Technology, Orsay, FRANCE.

There is a strong demand for PZT sol-gel precursors that will simplify greatly the technological process of preparation of thin and 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, actuators?). 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 needed prior to densification. A hybrid sol has been developed that 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 prepared in one deposit with these sols without cracks. 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 400 $\mu\text{m}$  squares was made and a final 0.6 $\mu\text{m}$  thick PZT has been obtained with no cracks and a very good adhesion on silicon with Pt electrode. These sols give also a very high yield in PZT oxide. Sols 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 effluent 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)

Chairs: 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-GEL THIN FILMS. Jeffrey I. Zink,  
Raquel Hernandez, Anne-Christine Franville, Payam Minoofar, Bruce  
Dunn, Department of Chemistry and Biochemistry, University of  
California, Los Angeles, CA.

Three strategies for placing molecules in deliberately chosen regions of mesostructured thin films made by the sol-gel dip-coating 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 regions: the silicate framework, the organic region formed by the hydrocarbon tails of the surfactants, and the intervening ionic interface formed by the 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 luminophores. 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 places lanthanide complexes into the silica framework via co-condensation of a silylated 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 silica framework via the silylated 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 HYBRID MATERIALS BY NANOSCALE CHEMISTRY  
AND NANOPHOTONICS. Jean-Pierre Boilot, Sophie Besson, Valerie  
Buisson, Frederic Chaput, Thierry Gacoin, Arnaud Huignard,  
Nathalie Landraud, Jacques Peretti, Physique de La Matiere  
Condensee, UMR CNRS 7643, Ecole Polytechnique, Palaiseau Cedex,  
FRANCE; Sophie Besson, CNRS/Saint-Gobain, UMR CNRS 125,  
Aubervilliers, FRANCE; Christian Ricolleau, Laboratoire de  
Mineralogie Cristallographie, UMR CNRS 7590, Paris 6 et 7, Paris  
Cedex 05, FRANCE.

We present different arrangements of hybrid nano-dots for optical applications: - Highly concentrated luminescent colloids II-VI quantum dots,  $\text{YVO}_4:\text{Ln}$  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  $\text{YVO}_4:\text{Ln}$  nanocrystal-silica composites. - 3D random networks of quantum dots are prepared by gelation of colloids. As in the silica system, the transparent percolating structure can be described as homogeneous assemblies of fractal clusters whose sizes are inferior to visible-range wavelength. - 3D 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 can be extended at a large scale on different substrates. These high density arrangements of nanocrystals are required in different applications such as semiconductor lasers. - 2D dense arrays of nano-dots are optically inscribed by using near-field optical patterning of photochromic azo-hybrid films with subwavelength resolution. This provides potential applications to optical lithography and high density optical data storage with a capacity of at least 1  $\text{Go}/\text{cm}^2$ .

**9:30 AM Q11.3**

OPTICAL RESPONSE OF DENDRIMER-ENCAPSULATED CdS  
QUANTUM DOTS IN SOLUTION AND IN THIN  
FILMS—REGULATION OF INTER-PARTICLE ELECTRONIC  
COUPLING. D.D. Richardson, S.R. Ely, 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 those studies of metal nanoparticles to understand optical response observed in collections of semiconductor nanoparticle (CdS quantum dots). Absorption and photoluminescence measurements have been combined with TEM and dynamic light scattering and with our understanding of related 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 bandshifts and changes in quantum efficiency. Some of these changes are predicted on the basis of our study of the metal-containing systems, but some of the results are rather surprising at first glance. The terminal functional groups on the dendrimers play a key role in determining the extent of these effects. The results of this study will allow us 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 PHOTOPATTERNABLE  
DIELECTRICS FOR MULTILAYER MICROWAVE CIRCUITS.  
Lothar Froehlich, Ruth Houbertz, Stephane Jacob, Michael Popall,  
Fraunhofer-Institut fuer Silicatforschung, Wuerzburg, GERMANY;  
Roland Mueller-Fiedler, Juergen Graf, Robert Bosch GmbH,  
Gerlingen-Schillerhoehe, GERMANY; Marco Munk, Marconi  
Communications GmbH, Backnang, GERMANY; Hasso von  
Zychlinski, UnaveraChemLab, Mittenwald, GERMANY.

Inorganic-organic hybrid polymers (ORMOCERs) combine very good optical and dielectric properties in the lower high frequency range ( $\epsilon_r = 3.1$  and  $\tan\delta = 0.004$  at 1 MHz). This is particularly promising for electro-optical applications<sup>1</sup>. 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  $\epsilon_r < 3$ , a dielectric loss  $\tan\delta$  of about  $10^{-3}$  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 high frequency applications, which can be prepared as coatings as thick as 150  $\mu\text{m}$  and additionally be patterned by UV lithography with sufficient lithographic resolution. Therefore, the synthesis of novel ORMOCER resins starts from styrene-substituted organosilanes and silanediols as precursors reacted by sol-gel-processing in combination with organic crosslinking of polymerizable 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  $\epsilon_r = 2.5$  and  $\tan\delta = 0.004$ .

<sup>1</sup> M. Popall, A. Dabek, M.E. Robertsson, S. Valizadeh, O.J. Hagel, R. Buestrich, R. Nagel, L. Cergel, D. Lambert and M. Schaub; *Mol. Cryst. and Liq. Cryst.* 354, 123-142, 2000.

**10:15 AM \*Q11.5**

FROM CONDUCTING POLYMERS TO HYBRID ELECTRO-  
ACTIVE MATERIALS. Pedro Gomez-Romero, Instituto de Ciencia  
de Materiales de Barcelona (CSIC), Bellaterra, SPAIN.

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

**10:45 AM \*Q11.6**

USE OF SOL-GEL HYBRIDS FOR LASER OPTICAL THIN FILMS.  
Philippe Belleville, Philippe Prené, Claude Bonnin, Yves  
Montouillout, CEA/Le Ripault, Monts, FRANCE.

The CEA/DAM megajoule-class pulsed Nd:glass laser devoted to Inertial Confinement Fusion (ICF) research is requiring 7,000-m of coated area onto 10,000 optical components. Among these different optics, two specific examples of applied sol-gel chemistry will be described. First one is dealing with the 240 44-cm square cavity-end mirrors needing to be highly-reflective (HR)-coated onto deformable substrates. Such mirrors are using stacks of SiO<sub>2</sub> and ZrO<sub>2</sub>-PVP (PolyVinylPyrrolidone) thin films, both starting from sol-gel colloidal suspensions (sols). The ZrO<sub>2</sub>-PVP high index layer is a nano-composite material prepared from mixing nanosized-zirconia 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-curing of the nanocomposite 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 highlight chemical interactions and polymer modifications under UV-irradiation. The as-developed HR-coating 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 ormosil 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 glow-discharges exposure with the lowest possible change in the reflection value. To fulfill these requirements, the hybrid material acts as an oxidation barrier, is chemical- and scratch-resistant, is durable and remain transparent in the 400-1000nm range. Moreover, the sol-gel process allows coating deposition onto large-sized and multi-shaped 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.

Chai-Won Kwon, Armel Poquet, Stéphane Mornet, Guy Campet, Josik Portier, Institut de Chimie de la Matière Condensée de Bordeaux, Cedex, FRANCE; A. Vadivel Murugan, B.B. Kale, Center for Materials for Electronics Technology, Ministry of Information Technology, Govt. of India, Panchwati, Pune, INDIA; K. Vijayamohan, National Chemical Laboratory, CSIR, Pune, INDIA; Jin-Ho Choy, National Nanohybrid Materials Laboratory, School of Chemistry, Seoul National University, Seoul, SOUTH KOREA.

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 bi-dimensional (lamellar) transition metal oxide. We choose conductive polymers as an organic component for high electric conductivity and transition metal oxides as an inorganic counterpart for large capacity and processibility. Polypyrrole/maghemite and poly(3,4-ethylenedioxythiophene) (PEDOT)/vanadium pentoxide hybrids were prepared and compared with their pristine materials for core-shell and intercalation strategies, respectively. Polypyrrole/maghemite showed an enhanced electrochemical reversibility and capacity up to 270 mAh/g in the potential range between 1.3 and 4.3 V vs. Li at 8 mA/g. PEDOT/vanadium pentoxide also exhibited improved reversibility and capacity up to 328 mAh/g at 15 mA/g between 2.0 ~ 4.4 V vs. 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 metals, doped character of the polymer and the nature of interaction between the polymer and the transition metal oxides.

#### 11:30 AM Q11.8

OPTICAL PROPERTIES OF CONJUGATED OLIGOMER 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 materials. Mesostructured materials (inorganic/surfactant composites) are typically prepared using a one-step synthesis procedure where the inorganic/surfactant/optically active species co-assemble. The simultaneous co-assembly leads to improvements in optical characteristics by allowing high doping concentrations while at the same time maintaining high dispersion to avoid concentration quenching. These composites have previously been shown to be high gain materials that display low threshold amplified spontaneous emission (ASE) and lasing. While significant progress has been made in producing dye-doped mesostructured

materials, little progress has been made in doping mesostructured materials with luminescent polymeric or oligomeric compounds. These types of extended molecules are especially interesting with respect to possible control over orientation of the polymer/oligomer chain by the long range ordering present within the mesostructures. Here we report on the synthesis and optical properties of mesostructured silica/ block-copolymer materials doped with water-soluble polymers and oligomers.

#### 11:45 AM Q11.9

DISSIPATIVE FORCED-INTRUSION OF WATER IN HYDROPHOBIC POROUS SILICA: A NEW FIELD OF APPLICATIONS FOR MCM-41 TYPE MATERIALS. B. LeFevre\*, E. Charlaix\*\*, P.F. Gobin\*, J.F. Quinson\*, G. Vigier\*. \*Groupe d'Etudes de Metallurgie Physique et de Physique des Matériaux, Villeurbanne, FRANCE. \*\*Dept de Physique des Matériaux, Villeurbanne, FRANCE.

A new type of mechanical applications has been highlighted for micro and mesoporous lyophobic materials [1]. For instance, by forcing water (non-wetting liquid) to invade a hydrophobic porous solid by means of an external pressure, mechanical energy can be converted to interfacial energy. The capillary pressure,  $P_{CAP}$ , required for pore intrusion can be written from the Laplace-Washburn relation,

$$P_{CAP} = - \frac{2\sigma \cos\theta}{r}$$

$\sigma$  being the liquid surface tension,  $r$  the pore radius and  $\theta$  the contact angle between the liquid and the solid. This stored energy can then be completely [2] or partially restored once the system recovers the initial extruded state. This former case was considered: actually, the extrusion pressure is lower than the intrusion one. This hysteresis is the cause of energy dissipation. Applications of such systems would be shock absorbers, dampers... Anterior studies [3][4][5] demonstrated the efficiency of hybrid organic-inorganic materials for such applications: from these results obtained using grafted silica gels, surface chemistry and porous texture were found to control this phenomenon.

Our presentation will focus on the use of model materials, highly hydrophobic grafted MCM-41 materials obtained from collaborators [6]. Two particular properties were underscored using that kind of supports: firstly, due to their unique textural properties, (cylindrical pores) quasi-constant intrusion pressure has been observed. Secondly, very high extrusion pressure has been obtained, which had never been reported before for hydrophobic mesoporous materials [7]. These two improvements allow such a technology to best fit the schedules of conditions of potential operational dissipative devices. The variation of experimental parameters (pore size, grafting agent, temperature and liquid type) allowed to achieve a better comprehension of the mechanisms. For instance, it is worth noting that strong analogies exist with capillary condensation: the hysteresis also appears to depend on pore size and temperature. A synthesis will be presented.

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#### SESSION Q12: PROPERTIES OF HYBRIDS (OPTICAL, ELECTRICAL, MECHANICAL, CATALYSIS)

Chairs: Thomas Bein and C. Jeffrey Brinker  
Friday Afternoon, April 5, 2002  
Metropolitan II (Argent)

#### 1:30 PM \*Q12.1

CHEMORHEOLOGY AND MECHANICAL PROPERTIES IN RELATION TO THE MORPHOLOGIES OF HYBRID ORGANIC-INORGANIC MATERIALS: A REVIEW. Jean-Francois Gerard, Hamid Kaddami, Laboratoire des Matériaux Macromoléculaires LMM/IMP UMR CNRS 5627, INSA Lyon, Villeurbanne Cedex, FRANCE; Laboratoire de Chimie Organique

This paper propose a review of the literature on the relationships between morphologies and mechanical properties of organic-inorganic nanocomposites synthesised 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) behaviours 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, polymerisation temperature, and pH of the reaction medium, dispersed inorganic-rich phase or co-continuous organic-rich and inorganic-rich phases, nature of the interactions at the organic-inorganic interface), ii/ the route for processing the hybrid O/I materials from hydrolysis and condensation reactions (in the polymer solution combined with drying, simultaneous polymerisation of metal alkoxides and organic monomers or from metal alkoxide-terminated organic oligomers). The analysis of the rheological changes during the synthesis, i.e. chemiorheology of the reactive system, contribute to a better knowledge of the generated morphologies.

#### 2:00 PM \*Q12.2

**HYBRID CATALYTIC NANOSTRUCTURES.** Thomas Bein, Jake Reder, Chris Huber, Dirk De Vos, Steven B. Ogunwumi, Langqiu Xu, Department of Chemistry, University of Munich, Munich, GERMANY.

In this presentation we will discuss different strategies for the incorporation of catalytic activity into microporous and mesoporous nanostructures. Such strategies include grafting or encapsulation of selective molecular catalysts and sequential redox cycles of encapsulated species. Typical examples include metal oxide clusters and metal coordination complexes in zeolite hosts, metal alloys and grafted chelate complexes in mesoporous materials, and enantioselective chiral catalysts encapsulated in porous hosts. Mass transfer in and out of the channel system is controlled by the sorption properties and the structure of the channels. Control of morphology permits the development of thin film formats for efficient activity assays. Thus, catalysts and catalyst precursor complexes were covalently attached to high surface area, accessible mesoporous films of various types (with thickness of up to 1000 nm) that 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 glycidoxypropyl-trimethoxysilane, followed by covalent grafting of porphyrin complexes such as tetrakis-(2-aminophenyl)-Zn porphyrin. These catalyst-containing mesoporous nanostructures exhibit activity in selective catalytic oxidation reactions, thus demonstrating the enormous versatility of porous hosts for the design of functional hybrid systems.

#### 2:30 PM Q12.3

**PARTICLE DOPED ORGANIC-INORGANIC HYBRID COATINGS AS CORROSION INHIBITING SURFACE TREATMENTS FOR ALUMINUM ALLOYS.** Tammy L. Metroke, Olga Kachurina, Edward T. Knobbe, Oklahoma State University, Environmental Institute, Stillwater, OK.

Hybrid organic-inorganic films (Ormosil) have been found to provide good corrosion resistance for metal substrates and are potential replacement systems for hexavalent chromium conversion coatings. In this study, sub- to micron-sized particles (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiC, TiN) were found to significantly enhance the corrosion protective properties of the Ormosil coating as determined using electrochemical and accelerated salt spray methods. Structure-property relationships are being investigated to understand the observed corrosion resistance characteristics.

#### 2:45 PM Q12.4

**POLYMER-ZEOLITE NANOCOMPOSITE MEMBRANES FOR GAS SEPARATION.** Huanting 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 crystalline 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 of these studies use rather large zeolite particles (e.g., micrometers). And there is no successful example of polymer-zeolite composite membranes with high selectivity so far because of interfacial 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 into polymer matrix zeolite nanocrystals with good dispersibility in organic solvent that is compatible with polymer matrix, helping eliminate interfacial defects of composite membranes. Colloidal 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 has proven unsuitable for colloidal zeolite nanocrystals because it leads to severe irreversible aggregation. We have very recently developed a novel technique for the preparation of redispersible zeolite nanocrystals in solvents [1]. This kind of re-dispersible template-free zeolite nanocrystals is promising for membrane application. In this presentation, we will show our efforts in detail on the preparation and characterization of zeolite nanocrystals (e.g., silicalite 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.

1. Huanting Wang, Zhengbao Wang, and Yushan Yan, Colloidal suspensions of template-removed zeolite nanocrystals, Chem. Commun., 2000, 2333-2334.

#### 3:00 PM Q12.5

**POLYSILANE-BASED THIN FILMS WITH HIGH PHOTOSENSITIVITY.** Gregory M. Jamison, Kelly Simmons-Potter, B.G. Potter, Jr., Carol C. Phifer, Sandia National Laboratories, Albuquerque, NM.

A great deal of research has been done to understand the photo-sensitive optical response of inorganic glasses, which exhibit a permanent, photo-induced refractive index change ( $\Delta n$ ) due to the presence of optically active point defects in the glass structure. In the present work, we have investigated the intrinsic photosensitivity of a family of poly(aryl)(methyl)silanes and poly(diaryl)silanes for use in photonic waveguide devices. Limited testing of passive optical behavior (e.g. absorption, refractive index), photosensitive response, and thermal behavior was performed for our material in thin film form. It was determined that the materials exhibited dramatic photobleaching 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 estimated. Confirmation of this calculation has been provided via ellipsometry which estimates refractive index changes at 632 nm of  $-0.14 \pm 0.01$ . In addition, embedded strips have been photoimprinted 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 multiprogram 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 OLIGO(PHENYLENEVINYLENE)S WITH ALKOXYSILANE END GROUPS.** Heiner Detert, Erlk Sugiono, Johannes Gutenberg-University, Mainz, GERMANY.

Due to their strong fluorescence, stilbenoid oligomers are one of the preferred classes of luminescent materials for electrooptical applications. The good solubility of alkoxy-substituted 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 only poor. This paper presents the synthesis of monodisperse oligo(phenylenevinylene)s with curable units, either terminal vinyl groups for thermal cross-linking or alkoxy silane moieties for curing via siloxane bridging. The alkoxy silanes are rigidly connected to the chromophores via Heck reactions or cross-metathesis with vinylalkoxy silanes. Hydrolysis and subsequent condensation yields oligosiloxanes with pendent OPVs, thus greatly improving the film forming capability of these materials with well defined chromophores. The connection to cyclosiloxanes or siloxane networks 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 functionalised with alkoxy silane groups. These compounds 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.** Lahcène Ouahab, Stéphane Golhen, F. Iwatori, Université de Rennes 1, FRANCE; Akira Miyazaki, Toshiaki Enoki, T.I.T, Tokyo, JAPAN; Jun-ichi Yamada H.I.T., Himeji, JAPAN.

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  $\pi$ -d interactions. In order to match 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 quanted 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  $\pi$ ligands 2.- We present novel molecular bricks, namely  $[M(\text{hfac})_2](\text{TTF-py})_2$ ,  $M = \text{Cu}^I, \text{Mn}^I$ , hfac= hexafluoroacetylacetonate; TTF-py= 4-(2-tetrathiafulvalenyl-ethenyl)pyridine in which the conducting and the magnetic systems are covalently linked through a conjugated bridge. L. Ouahab, Chem. Mat., 1997, 9, 1909. F. Iwahori, L. Ouahab, S. Golhen, J.P. Sutter, R. Carlier, Inorg. Chem., 2001, in press.

### 3:45 PM Q12.8

NEW INORGANIC-ORGANIC OPEN FRAMEWORK CHALCOGENIDES. Pingyun Feng, Cheng Wang, Xianhui Bu, Nanfeng Zheng, Yuqi 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

NANOSTRUCTURAL ENGINEERING AND CRYSTALLISATION OF TITANIA THIN FILMS. C.J. Barbe, S.L. Cram, J.R. Bartlett, D.J. Cassidy, D.R.G. Mitchell and K.S. Finnie, ANSTO, Materials Division, Lucas Heights Research Labs, Menai, AUSTRALIA.

Sol-gel chemistry provides the "nanostructural engineer" with a range of nanosized precursors for the production of thin films with tailored properties. In this study, we have investigated the structural evolution of thin titania films prepared from three types of sol-gel precursor:

- Polymeric titania sols, prepared by controlled hydrolysis of titanium butoxide at pH 1;
  - Stable nanoparticles (~ 5 nm) prepared by hydrolysis of acetylacetonate-modified titanium isopropoxide and subsequent peptisation at pH 2;
  - Ordered oxo-organo titanium (IV) clusters (including  $[\text{Ti}_6\text{O}_4](\text{OR})_8(\text{OOR}')_8$  and  $[\text{Ti}_6\text{O}_6](\text{OR})_6(\text{OOR}')_6$  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-organo 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